CHEMICAL REVIEWS

pubs.acs.org/CR

Review

# Polymers without Petrochemicals: Sustainable Routes to Conventional Monomers

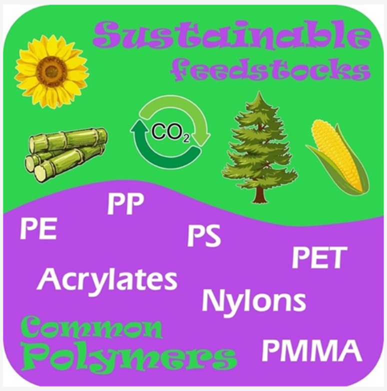
Graham Hayes, Matthew Laurel, Dan MacKinnon, Tieshuai Zhao, Hannes A. Houck, and C. Remzi Becer*

**Cite This:** https://doi.org/10.1021/acs.chemrev.2c00354

Read Online

ACCESS | Metrics & More | Article Recommendations

**ABSTRACT:** Access to a wide range of plastic materials has been rationalized by the increased demand from growing populations and the development of high-throughput production systems. Plastic materials at low costs with reliable properties have been utilized in many everyday products. Multibillion-dollar companies are established around these plastic materials, and each polymer takes years to optimize, secure intellectual property, comply with the regulatory bodies such as the Registration, Evaluation, Authorisation and Restriction of Chemicals and the Environmental Protection Agency and develop consumer confidence. Therefore, developing a fully sustainable new plastic material with even a slightly different chemical structure is a costly and long process. Hence, the production of the common plastic materials with exactly the same chemical structures that does not require any new registration processes better reflects the reality of how to address the critical future of sustainable plastics. In this review, we have highlighted the very recent examples on the synthesis of common monomers using chemicals from sustainable feedstocks that can be used as a like-for-like substitute to prepare conventional petrochemical-free thermoplastics.

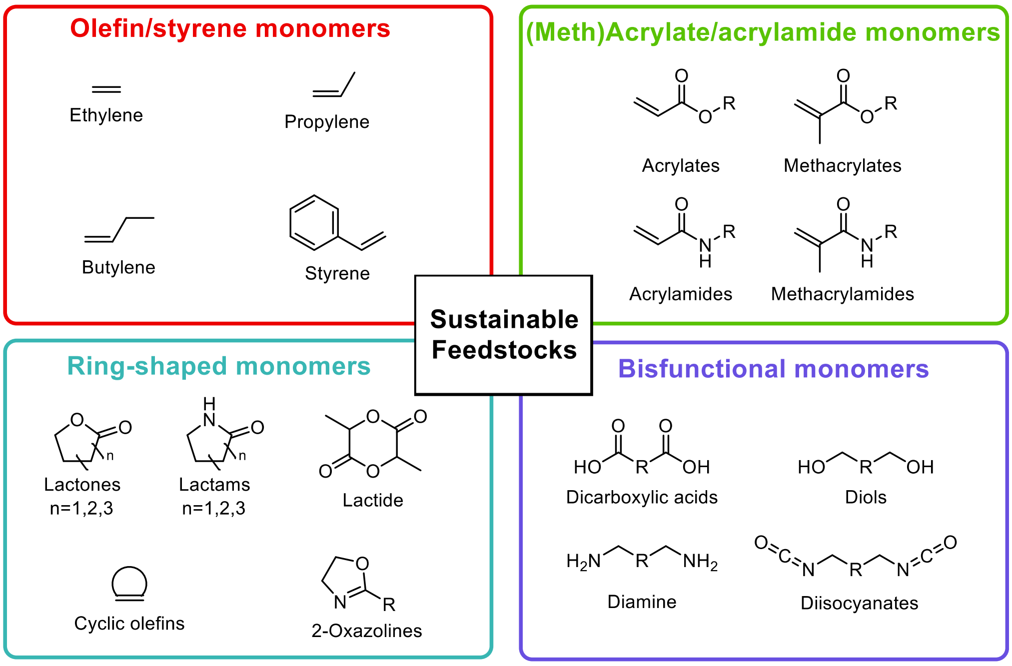


## CONTENTS

**Special Issue:** Sustainable Materials/Sustainability

**Received:** May 31, 2022

**Scheme 1. Overview of the Four Sections in This Review Article That Are Categorized Based on the Types of Monomers That Are Obtained from Sustainable Feedstocks and Used in the Synthesis of Commodity Thermoplastics**



## 1. INTRODUCTION

The amount of plastics produced ever worldwide has exceeded 8.3 billion metric tons and a large proportion of these materials has ended up in a landfill.[1] Owing to the excellent chemical stability of plastic materials and their low degradation rates in the environment, the accumulated plastic waste in landfills and marine environments has become more and more noticeable over the last decade.[2] Thus, degradation analysis over prolonged periods has become possible and the influence of key parameters such as crystallinity and hydrophobicity can be studied alongside the chemical structures and toxicity of resulting plastic degradation products.[3,4] Bio-based polymers that are degradable are considered to be a solution for the landfill waste and have been reviewed widely in the literature.[2,5−9] However, the process of creating new plastics and establishing their life cycle analysis is long, costly and risk-taking for the chemical industry.[10] Moreover, material properties of newly invented plastics are often inferior to those of established thermoplastics, making it difficult to compete with conventional technologies. Therefore, the chemical companies and the plastic industry remain reluctant toward the introduction of completely new plastic materials and typically maintain a more conservative approach in marketing plastics with completely new chemical structures even if they can be fully obtained from sustainable resources.[11]

Renewable resources such as lignocellulose, vegetable oils, terpenes and carbohydrates are used as feedstocks for the synthesis of sustainable polymers.[12−14] Biomass has been used to produce hundreds of value-added compounds that are further used in the synthesis of polymers.[15−18] However, most of these polymeric structures are novel polymers with new chemical compositions in comparison to common plastics. Therefore, it would require a significant capital investment to commercialize any of these novel polymer structures as sustainable polymers. On the other hand, using cost-competitive sustainably sourced monomers in cemented manufacturing processes would enable the synthesis of known polymeric structures and hence sustainable plastics in a timely manner. As this implies creating the same plastic with the same chemical composition, there is no requirement of registering such conventional polymers or applying for safety certificates from regulatory authorities such as the Food and Drug Administration (FDA) and Environmental Protection Agency (EPA).[4,19,20]

With the increasing fuel prices and geopolitical dependence, the research on finding new chemical resources to create commodity plastics without using petrochemical derived chemicals is expanding on an exponential scale. Most reviews on sustainable polymers are focused on a particular bio-based feedstock from which an array of monomers and materials can be prepared. Instead, this review is centered around the specific monomer classes that are used in conventional polymerizations and summarizes routes to access these from renewable resources. We have categorized the sustainable building blocks in four groups, i.e., olefins/styrenics, (meth)acrylics, cyclic monomers and commonly used bifunctional monomers that are used in step-growth polymerization (Scheme 1). The main aim of this review is to present a roadmap toward bio-sourced monomers that could be considered in order to replace

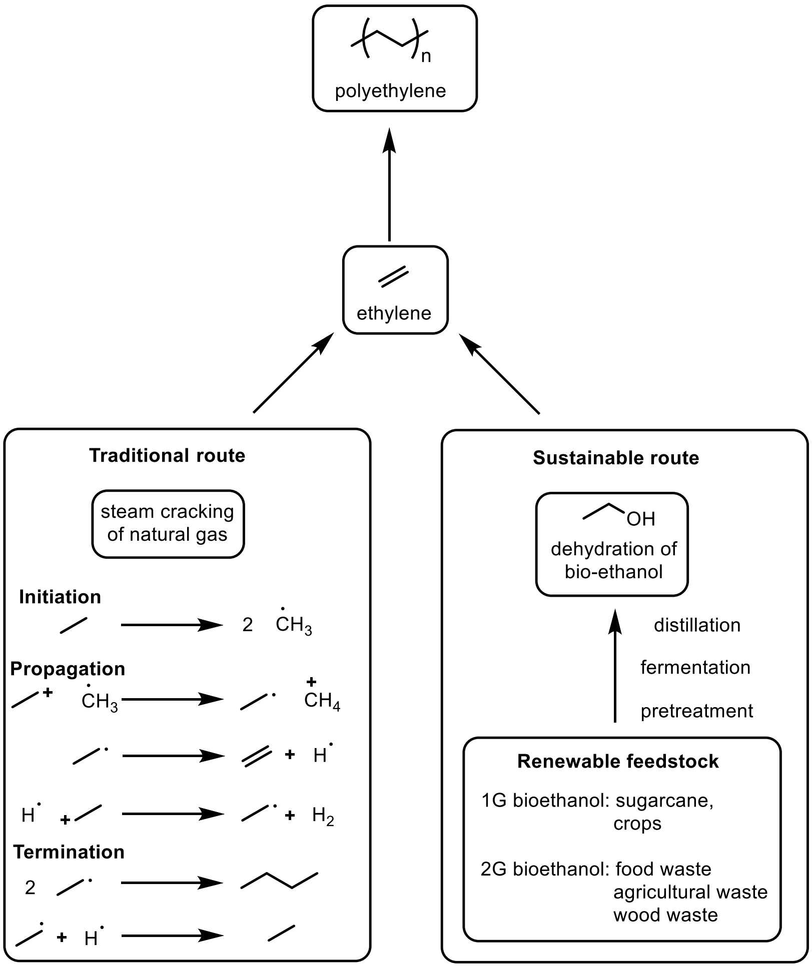


**Figure 1.** Polyethylene from the traditional way and the sustainable way.

petrochemically derived bulk monomers that are currently used in the production of commodity plastics, on a like-for-like basis. The first section is describing the synthetic routes to obtain olefins and styrenics used as building blocks in the production of polyethylene (PE), polypropylene, polybutylene and polystyrene. The main chemical that is used to create PE is bio-sourced ethanol and sustainable bioresources and its chemical dehydration process to ethylene have been highlighted. The following section is focusing on the (meth)acrylics and (meth)arylamides monomer classes. There is a large variety of acrylic polymers, of which the most widely used and commercially available polymeric structures have been discussed. The next section is based on ring shaped cyclic monomers mainly to create polylactones, polylactams and polylactides (PLA). This category is specifically important as PLA has become one of the most popular plastics materials for single use applications. In the final part, we have focused on the range of bisfunctional monomers that are used in the synthesis of some important step growth polymers such as polyesters and polyamides. While there are many other functional groups (e.g. epoxides) or multifunctional ($f \geq 3$) derivatives that are receiving increased attention for the formation of thermosets, we have directed our focus to those most widely used in the synthesis of commodity thermoplastics.

## 2. OLEFIN AND STYRENIC MONOMERS

Polyolefins derived from olefin monomers have a broad range of industrial applications as a result of their outstanding properties such as transparency, gas permeability, heat and chemical resistance.[21−24] Hence, polyolefins are commonly used in plastics for food storage, packaging, piping and clothing.[25] In 2015, polyolefin materials constituted 45% of the consumer plastics and half of those produced,[21] while it was reported in 2018 half of the global plastic market consisted of polyolefins.[26] The two most used polyolefins are polyethylene, which includes both low and high density polyethylene, and polypropylene that dominates in the dairy packaging and plastic hinge production.[25] However, this continuous cycle of production and consumption has led to plastic waste becoming a significant issue.[21] The stability of polyolefin materials causes extremely slow degradation of these materials, and combustion of polyolefins leads to the problem of releasing additional volitale organic compounds (VOCs) that can contribute to climate change. It was estimated that only around 20% of plastics used since 1950 are recycled while the rest either end up in landfill or remain unaccounted for, which leads to terrestrial and aquatic "white pollution".[21,26] The consumption of non-renewable petrochemical resources to make olefin monomers for the preparation of polymers is also massive, constituting 5% of petroleum and natural gas resource consumption. Stemming from growing concerns regarding global climate change, the use of fossil-fuel resources is being

Table 1. Examples of Reported Renewable Feedstocks for Bioethanol Production

| Feedstock | | Yield to sugar (g/g) | Conversion to sugar (%) | Productivity (g/L h) | Max. concentration (g/L) | Ref. |
|---|---|---|---|---|---|---|
| Agricultural products | Bamboo shoots | 0.169 | 98 | | | 57 |
| | Coconuts and cactus | | 90.09 | 0.21 | | 58 |
| | Cassava | | | | 35.01 | 59, 60 |
| | Corn[a] | | | | | 37−39, 61 |
| | Potato[b] | | | | | 62 |
| | Sugarcane[c] | | | | | 32−34, 36, 48 |
| | Sugar beet | | | | 132.39 | 63 |
| | Sweet sorghum | 0.47 | | | 82 | 56, 64−66 |
| | Wheat | | | | 132.1 | 38, 67 |
| | Sweet potato | | | | 38 to 100 | 41, 55 |
| | Paper mulberry fruit juice | 0.48 | | 4.7 | 73.69 | 68 |
| Food wastes | Banana peel[d] | | | | | 69 |
| | Cashew apple pulp | 5 | 46 | | | 70 |
| | Coffee pulp | 0.46 | 40 | | | 70 |
| | Pineapple waste | | 96 | | | 40 |
| | Potato waste | 0.32 | | | 22.54 | 71−73 |
| | Sugarcane juice | | | | 42.1 | |
| | Sweet potato waste | 0.46 | 47 | | 79.00 | 41, 55, 71 |
| | Brewery waste | | | | 219 | 74 |
| | Coconut | 20% v/v | | | | 75 |
| | Mandarin peels | 50−60 L/t | | | | 43, 76 |
| | Citrus wastes | 93.1% | | | 14.4 to 29.5 | 77 |
| | Olive mill solid | | 3 | | | 78 |
| | Seaweed | 84.9% | | | 25.7 | 79, 80 |
| | Waste hamburger | 0.271 | | | 27.4 | 81 |
| | Pomegranate peel | 0.50 | | 0.99 | 14.35 | 82 |
| Agricultural wastes | Banana pseudo stem | | | | | 83 |
| | Sugarcane bagasse | 102 L/t | 84 | 0.024 | 17.1 | 49, 51, 84, 85 |
| | Sweet sorghum bagasse | 0.48 | 81 | 0.59 | | 64 |
| | Vineyard waste | | 13.1 | | | 86 |
| | Grape pomace | 0.419 | 82.1 | | | 87 |
| | Corn Stover | 330 L/t | | | | 61, 88−93 |
| | Cotton stalk | 52% | | | 47.0 | 90, 94, 95 |
| | Sesame plant | | | | 1.90 | 96 |
| | Rice straw | 61.3% | | | 29.1 | 97−99 |
| | Wheat straw | 0.39−0.42 | 68−76 | | | 100, 101 |
| | Grass biomass | 32.7%−95% | | | 4.72−32.1 | 102, 103 |
| | Banana frond juice | 0.33 | | | 45.75 | 104 |
| Wood wastes | Acacia wood | | 90 | | | 105, 106 |
| | Apple wood | | 70 | | | 107 |
| | Eucalyptus globulus wood | | | | 93 | 108, 109 |
| | Fir wood | | | | 43.96 | 45 |
| | Hornbeam wood | 251 L/t | | | | 110 |
| | Japanese cedar wood | | 1.7−30 | | | 111 |
| | Pine wood | | 44 | | | 105, 112 |
| | Sengon wood | | 18 | | | 44 |

[a] Over 4.38 billion bushels of corn was used to produce over 68 billion L of ethanol in the US in 2016. [b] Low concentration of bio-EtOH produced. [c] Commercialized 1G bioethanol production. [d] Different pretreatment techniques have been studied using same acidic hydrolysis procedure. It was shown that acid pre-treatment give rise to highest reducing sugar concentrations but did not guarantee a highest bioethanol concentration.

thoroughly revised. As commodity polyolefin plastics remain undervalued in our society and hence facilitate plastic pollution, the development of methods to prepare "bio-labelled" polyolefins in sustainable ways from renewable resources has attracted significant research attention.[21,23,24,27−29]

While preparing bio-based polyolefins, several factors should be considered to maximize their sustainability. As highlighted by Siracusa and Blanco,[21] there are three standards for bioplastics. First, the monomer used in the polymerization should be fully or partially derived from biological sources. This is to prevent any competition with the food chain and ensure food security for animals and humans. Second, the preparation strategy should be energy efficient, non-hazardous and produce minimal waste. Finally, the resulting polymeric material should be, ideally, chemically or mechanically recyclable or degradable under biological or chemical conditions, ideally mild ones, for example by being compostable with low or no hazardous residue. One good example of the chemical or mechanical recycling of bio-plastics is a recent report on polyethylene-like material prepared by Häussler et al, where the bio-plastic reported was chemically degradable under 120 °C in basic ethanol.[30] However, the degradation behavior depends on the stability of the chemical structure of the polymer, which also largely determines their mechanical and thermal properties. Thus, high degradability for hydrocarbon polymeric materials with stable structures such as polyethylene may prove unattainable. In reality, it is difficult to achieve all these standards simultaneously, and as long as polymers fulfill one of these criteria, they are typically considered bio-plastics.[21,22,25] For bio-polyolefins, the first criteria regarding the bio-based monomer feedstock is the most commonly fulfilled. This section will focus on existing work on the synthesis of bio-based olefin monomers, as well as their use of feedstock for the preparation of its corresponding commodity plastic materials.

## 2.1. Ethylene

Polyethylene, the most used polymer in the world, represents more than 30% of the global plastic market and is produced in several forms including low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE).[21] PE is a homopolymer of the monomer ethylene, which is mostly obtained as a distillation product of petroleum. Conventionally, ethylene is prepared via the thermal cracking of hydrocarbons under 750−1000 °C in catalytic reactors.[21,24,31] As PE is widely produced and consumed, the amount of petroleum sources used for the polymer production has raised concerns on non-renewable energy sources. Hence, the approach of deriving renewable ethylene monomers from bio-ethanol has been widely employed as the current solution to the bio-production of ethylene in order to reduce the consumption of petroleum sources. Several biomasses such as sugarcane,[32−36] corn,[37−39] food waste[40−43] and wood waste[44−46] have been reported to be converted into bio-ethanol via procedures including pre-treatment, saccharification (or hydrolysis) and fermentation. The core actions in these processes are the extraction of polysaccharides and oligosaccharides from the feedstock and fermentation of the obtained sugars into ethanol. There are two classes of bio-ethanol (bio-EtOH): 1G bio-EtOH and 2G bio-EtOH.[32,47,48] 1G bio-ethanol is commonly used to refer to bio-EtOH derived from sugarcane or crop grains,[33,39,47,48] while 2G bio-EtOH is derived from lignocellulosic biomass.[49−51] As lignocellulosic biomass waste is produced in vast amounts and does not compete with food production, investigations into 2G bio-EtOH has become the main focus of new bio-ethylene production research. A comparison of ethylene preparation procedures via petroleum and biomass resources is shown in Figure 1. There are several general steps in the bio-production of ethylene, which are the pre-treatment of the bio-based feedstock, fermentation, distillation and catalytical dehydration, and these steps are discussed in detail in the following section.

**2.1.1. Renewable Feedstock for Bioethanol Production.** Bio-EtOH, the bio-based starting material for the bio-production of ethylene, can be obtained from various sources. Several reviews and reports have been published on different feedstocks used to produce 1G and 2G bio-EtOH, which can be employed for bio-ethylene production.[34,42,50,52−56] A summary of reported feedstocks, along with their conversion, is shown in Table 1.

Agricultural products like sugarcane are used to produce 1G bio-EtOH, and a range of other crops like potato and wheat have also been used.[32,34−39,48,55,62,67] Two main sources for 1G bio-EtOH production are sugarcane juice and molasses (as well as a third, corn); these two renewable feedstocks have been commercialized mainly in Brazil and the US.[33,36−39,47,52,61] Various sugars are obtained from the first two feedstocks *via* crushing and extraction with water, while glucose is obtained from corn feedstocks *via* the hydrolysis of starch in milled corn grains. Bio-EtOH production costs are low due to high yields of sugar obtained from the feedstocks and the high conversion of sugar to bio-EtOH. 1G bio-EtOH therefore is cost-efficient enough to be competitive with petroleum fuel.[35,51] Additionally, bio-EtOH production from sugarcane is reported to consume far less energy than from corn, explaining why ca. 25% of global bio-EtOH production is from sugarcane in Brazil.[34−36,113] The production of bio-EtOH from sugar has been widely investigated. For example, Morschbacker briefly reviewed the utilization of sugar as the feedstock for bio-EtOH production in Brazil in 2009, introduced the general conversion procedures, and highlighted the equipment used in the process.[114] In 2010, Dias *et al.* reported the improvement seen when using distillation and co-generation systems and performed simulated analyses producing 1G and 2G bio-EtOH from sugarcane with different pre-treatment methods.[48] Carvalho *et al.* analyzed the economic-energy-environmental factors of several bio-EtOH production programs from sugarcane, the illustrative results of which suggested the energy balance and gas emissions could be improved by using a combination of optimized production methods, including 2G bio-EtOH production.[34] The life cycle evaluation study by Luo *et al.* confirmed that a reduction in greenhouse-gas emissions was possible through producing bio-EtOH from sugarcane, when compared to conventional petrochemical feedstocks.[36] These works have highlighted the sustainability and promising potential of a sugarcane-based bio-EtOH market.

Corn is another renewable feedstock that has been commercialized for 1G bio-EtOH production, particularly in the US. More than 4.38 billion bushels of corn were used to produce over 68 billion liters of bio-EtOH in the US in 2016.[37,38] The life cycles of the bio-EtOH production systems of Brazilian sugarcane and US corn[24,34,36,37,39,47,51,52] were studied with different parameters, including the renewable energy ratio (RER), which was defined as the total renewable energy produced per unit of fossil energy consumed, and the greenhouse gas (GHG) emissions reductions. In both systems, high GHG emission reductions and high RER values were determined, supporting their sustainability aspect. Various research groups have reviewed the production of bio-EtOH from corn in detail.[24,37,38] In 2019, Kumar and Singh summarized the current status of bio-EtOH production from corn, with discussions on several factors like corn composition and structure, the bio-EtOH production from corn grains, corn stover and corn fiber, and technology advances in the corn-to-ethanol system.[37] Mohanty and Swain have also discussed the technological aspects of using corn as a renewable feedstock for bio-EtOH production and stated several advantages of the corn bio-ethanol system in a 2019 report.[38] They introduced the corn bio-EtOH production process from farm to fermentation, compared the dry-milling and wet-milling pre-treatment processes, and discussed several microorganisms used in the fermentation process. They also compared the corn bio-EtOH system with a possible wheat bio-EtOH production system from a technological perspective.

Apart from sugarcane and corn grains, other reported crops include wheat,[38] potato,[62] sweet potato,[55] cassava,[60] bamboo shoot,[57] sugar beet,[63,87,115] grape and cactus,[87] for which a range of pre-treatment processes and fermentation systems were employed. Fruit juices were also reported as potential bio-EtOH production systems with high EtOH concentrations reported.[68,75,104] For example, paper mulberry fruit juice was studied as a bio-EtOH feedstock by Ajayo *et al.*, where a high bio-EtOH concentration of 73.69 g $L^{-1}$, a high yield of 0.48 g $g^{-1}$ to sugar and high productivity of 4.7 g $L^{-1}$ $h^{-1}$ were recorded. The advantage of using food crops for bio-EtOH production is their usual abundance and low-prices in certain areas. Additionally, the by-product in the bio-EtOH production process can be recycled for crop fertigation, improving the sustainability of the route.[38,50,52,54] However, the main drawback of producing bio-EtOH with agricultural products is the possibility for competition with food crops, which triggers debate on the topic of food-versus-fuel and increases food prices and security concerns. Moreover, the production of bio-EtOH from crops is only competitive with petrochemical feedstocks in certain areas, which means the production would be localized and may not become a strong force in bio-EtOH production. Thus, a more generalized solution which avoids competition with food crops would be more advantageous for the future of the bio-EtOH industry.

During the production of bioethanol with sugarcane, a common side product is sugarcane bagasse, which is normally burnt to provide energy.[49,84,85] However, sugarcane bagasse also includes polysaccharides and has potential for utilization in bio-EtOH production.[85] It was first used to co-produce bio-EtOH to reduce the overall cost in the process of producing bio-EtOH with sugarcane.[48,51] To avoid competition with food crops, reduce the cost value of starting materials, and solve the environmental problem of agricultural waste, using polysaccharide-rich agricultural waste for bio-EtOH production was suggested as a practical solution. Crop residues like bagasse, stalk, straw and leaf wastes are the most common agricultural wastes and a variety of these have been reported as potential bioethanol production systems.[64,84,85,90,94,97−99,116] For example, sugarcane bagasse, the most common by-product of sugarcane harvesting and processing, has been subjected to techno-economic evaluation of its impact on biorefinery processes in different reports, and both integrated 1G and 2G bio-EtOH production systems and stand-alone 2G bio-EtOH production system have been studied.[48,49,51] For instance, Macrelli *et al.* has reported the study on 2G bio-EtOH production from sugarcane bagasse and leaves and integrated the production system with traditional 1G bio-EtOH production from sugarcane.[51] It was shown that with a yield of 102 L $ton^{-1}$ dry sugarcane with 50% leaves, the cost of bio-EtOH production could be reduced by about 50%. Other agricultural wastes have also been studied. Kadam and McMillan investigated the feasibility of bio-EtOH production with corn stover as a renewable feedstock in 2002 and pointed out about 80 million tons of dry corn stover could be available for bioethanol production.[88] Several reports have studied the production of bioethanol with only corn stover or with a mixed corn/corn stover system since then, with variations in several factors including pre-treatment method, corn stover varieties and solid loading.[61,88,90,93] Wheat straw and rice straw are another family of food crops residues and studies have shown the feasibility of producing bio-EtOH with these agricultural wastes.[100,101] Belal has reported the utilization of rotted rice straw residues for bio-EtOH production with optimization of pH and temperature for the microorganism mediated saccharification process.[98] The highest bio-EtOH concentration was reported after 7 days of fermentation as 11 g $L^{-1}$. Yoswathana and Phuriphipat studied bio-EtOH production from rice straw with different pre-treatment methods including acid treatment, alkali treatment and physical treatment, as well as enzymatic saccharification methods.[97] A combination pre-treatment method of acid and ultrasound followed by enzyme saccharification give rise to the highest bio-EtOH concentration, which was still lower than 15 g $L^{-1}$. Increasing rice straw loading for the bio-EtOH production may increase the yield and make the process more practical. Georgieva *et al.* reported the production of bio-EtOH with wet-exploded wheat straw in a continuous immobilized reactor system,[100] and an ethanol yield of 0.39 to 0.42 g $g^{-1}$ sugar was reported with conversion in a range of 68-76% from sugar. Another study by Tamburini *et al.* also achieved similar ethanol yield from sugar of 68%.[101] Comparison with other systems, the low yield of this system might prevent large-scale application. Other agricultural wastes including grass biomass,[102,103] sesame plant,[96] banana pseudo stem,[83] sweet sorghum bagasse,[64] vineyard waste,[86] cotton stalk[90,94] and coffee crop residue[117] were also reported to produce bio-EtOH with yields from sugar ranging from 6% to 95%.

Apart from agricultural wastes, food wastes also constitute a lignocellulosic content-rich feedstock with potential for bio-EtOH production.[42] It was reported that 1.3 billion tons of food wastes were produced each year, with landfill disposal both environmentally problematic and a waste of carbohydrate materials with huge potential.[42] Examples of studied food wastes for bio-ethanol production include pulp wastes from coffee,[117] apple pulp wastes,[70] banana[69,104,118] and peel wastes from mandarin,[43,76] banana[69] and potato.[72,73] For example, Chohan *et al.* reported bio-EtOH production from potato peel wastes utilizing the simultaneous saccharification and fermentation (SSF) method, with optimization of temperature, pH and solid loading.[73] With optimized conditions, the highest bio-EtOH concentration reached 22.54 g $L^{-1}$ with a yield to sugar of 0.32 g/g. Choi *et al.* studied bio-EtOH production from soybean waste (okara) and compared the bio-EtOH conversion from sugar of raw okara and pre-treated okara.[119] With the assistance of microorganisms, the concentration of bio-EtOH obtained could reach 59.1 g $L^{-1}$ with 96.2% conversion to sugar, which indicates okara might be a candidate for the high-yield production of bio-EtOH. A recent study from Han *et al.* investigated the usage of a waste hamburger as a bio-EtOH feedstock.[81] Enzymatic saccharification and fermentation methods were employed, with the hydrolysis rate shown to remain steady under increasing enzyme loading volumes, although higher bio-EtOH concentration could be achieved through increased enzyme loadings. Maximum bio-EtOH concentration was reported as 27.4 g $L^{-1}$, corresponding to 0.27 g/g waste hamburger. These studies illustrate the potential of using food wastes as bio-EtOH production systems. Due to the benefits of low cost and reducing the environmental impact of food waste, the sustainability of a food waste bio-EtOH system should appear promising.

Wood waste was recently developed as a renewable source for bio-EtOH production.[45,46] Large amount of carbohydrates

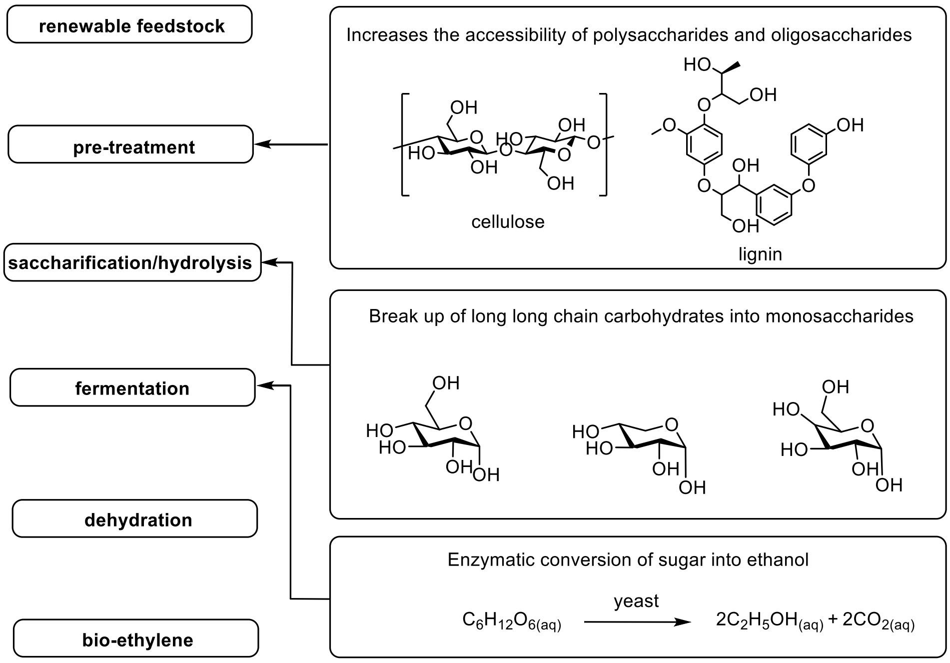


**Figure 2.** Steps of converting renewable feedstock into bio-ethylene.

including cellulose, lignin and hemicellulose are contained in wood wastes. Compared to agricultural wastes and food wastes, the higher density of wood waste results in lower transport cost, and the cultivation and harvesting of wood avoids competition with food production. Thus, wood and wood wastes such as sawdust, leaves and felled trunks were explored for their value in 2G bio-EtOH production. For example, acacia wood was studied by Lee *et al.* for the bio-EtOH production.[106] Alkaline pre-treated acacia wood was used for the production of bio-EtOH, and the yield of bio-EtOH to sugar was reported to be above 90%. Romani *et al.* reported the production of 2G bio-EtOH from steam-exploded *Eucalyptus globulus* wood.[109] A high bio-EtOH concentration of 51 g $L^{-1}$, which corresponds to 91% conversion from sugar, was reported. Although the autohydrolysis process used was high-temperature and energy-intensive, the high bio-EtOH concentration and conversion still indicate the potential of this system. Decent summarizing work has also been published in the field of bioethanol production from wood wastes.[45,46]

To summarize, various renewable feedstocks have been reported for both 1G and 2G bio-EtOH production. While considering the benefits of low-cost feedstocks, reductions in environment issues, and the maximum utilization of waste materials, bio-EtOH production from lignocellulosic wastes is attracting intense research interest and should have a promising future as novel solutions to bio-EtOH production.

**2.1.2. Monomer Preparation.** With a range of renewable feedstocks available for bio-EtOH production, a reliable procedure for the subsequent conversion of bio-EtOH to bio-ethylene is required for polymerization. In established studies, the procedure of producing bio-ethylene typically includes the pre-treatment of feedstock, saccharification (or hydrolysis), fermentation, distillation and catalytic dehydration (Figure 2). These steps will be herein introduced.

*2.1.2.1. Pre-treatment.* Pre-treatment is an important step in the production of bio-EtOH, as it can help break down lignin and glycosidic chains and increase lignocellulose digestibility.[67,102] The major objectives of the pre-treatment process are to reduce the physical size of the starting materials, to increase the accessibility of carbohydrates (hemicellulose, cellulose, lignin) to chemicals or enzymes in the hydrolysis step, to yield improved fermentable sugars, and to reduce the crystallinity of the cellulose matrix. Pre-treatment processes are highly recommended as they increase subsequent yields of the fermentable sugars, prevent premature degradation of the yielded sugars, and prevent the formation of inhibitors prior to hydrolysis and fermentation.[67,95,102,116] It was also reported that it lowers the demand of conventional energy in general. For example, in bulky renewable feedstocks like corn stover or wood, a pre-treatment step for physical size reduction is important to increase the total surface area of the material, allowing better accessibility for subsequent processing.[46,89,91,106,109] Simple mechanical pre-treatment is adequate for starch-based materials while chemical pre-treatment might be required for starting materials like wood, to help breaking the tough fiber structure and cell walls.[109,111,112,120] With smaller starting materials, easy hydrolysis methods like heating with water can be employed, which reduces the economic and energy cost of the overall procedure.[60] However, the bio-EtOH yield may vary with different methods of pre-treatment, influencing the balance of cost-efficiency versus maximum yield. Physical pre-treatment was predominantly reported for lignocellulosic starting material.[85,99] With additional pre-treatment methods, better hydrolysis conditions can be used in the following stage, and a better yield of sugars hydrolysis can be obtained.

Studies have also shown that bio-EtOH production is significantly impacted by the choice of pre-treatment.[76,82,92,94,102,111,116] Pre-treatment methods can be subdivided into biological, chemical, physical and physicochemical pre-treatment. Biological pre-treatment employs microorganisms to perform the pre-treatment task, which degrade the polysaccharide and oligosaccharide components of the feedstock to amorphous forms. Some typical microorganisms used for degradation of polysaccharides include brown rot, soft rot and white rot fungi.[111] While brown rot was able to degrade cellulose, soft and white rot were able to degrade both cellulose and lignin. Of these fungi, white rot fungi is considered to be the most favorable biological pre-treatment agent due to its ability to degrade polysaccharide and break the structure of lignin.[52] Biological pre-treatment is favorable due to its high sustainability, as only mild conditions are required during the process. Moreover, the innate ability of the fungi to degrade the lignocellulosic wall makes this process achievable without additional chemicals. Therefore, this can be considered the most sustainable approach. However, pre-treating the renewable feedstock by this method results in a slower production rate and reduced applicability to industrialized large-scale production. Combining biological pre-treatment methods with another efficient pre-treatment method may present a solution for the sustainable pre-treatment of lignocellulosic feedstocks for large scale bio-EtOH production.

Chemical pre-treatment is the process of adding supporting chemicals to break tough crystalline regions or cell walls, making the material more suitable for subsequent saccharification. It was believed to be the most suitable method for commercial scale production.[46,52,92,116,121] The advantages of using chemical pre-treatment include better availability and durability of chemical substances, lower cost and resilience toward technological developments (when compared to the enzymatic method, where engineered enzymes cost more than traditional enzymes). The chemical substances degrade the lignocellulosic walls and long-chain polysaccharides with chemical reactions that demand energy. Common chemicals used in the pre-treatment include acids and alkalis.[24,42,46,52,72,82,96,122] Several commercially available acids including hydrochloric acid, phosphoric acid, nitric acid, and sulfuric acid were used in acid pre-treatment, as well as several organic acids such as (per)acetic acid, maleic acid and lactic acid.[50,82,96] Acid pre-treatment can be performed either in a concentrated or diluted method. Concentrated acid pre-treatment requires short time-periods and mild temperatures, but often also results in the production of inhibitors and a reduction in bio-EtOH yield. Dilute acid pre-treatment leads to the same outcome as the concentrated acid pre-treatment, while dilute acid pretreatment does not require acid recovery with negligible acid loss. When compared to acid pre-treatment, alkali pre-treatment breaks more lignin component into a better accessible form for subsequent hydrolysis.[50,52,92,116] Sodium and potassium hydroxide are the most frequent alkaline solutions used in alkali pre-treatment.[92,106,116] Ammonia is also commonly employed as a pre-treatment agent in an attempt to produce 2G bio-EtOH.[89] Pre-treatment methods using ionic liquid fracture the non-covalent structure between hemicellulose, lignin and cellulose, caused by the strong hydrogen bond acceptors of the ionic liquid contained in chloride.[50] Although the suitability of ionic liquids with enzymes and fermentation microorganisms is still being investigated, ionic liquid pre-treatment is considered as a green, sustainable method.[42,54,114,123]

Another way to pre-treating the biomass is mechanically, where the size of biomass is physically reduced through cutting, chopping or other physical means. The aim is to decrease the biomass crystallinity, enhancing the remaining bio-EtOH production processes. For example, smaller-sized corn stover gave 1.5 times higher yield than a larger size corn stover substrate.[88,91,93] The most significant challenge for mechanical pre-treatment, however, is the significant power consumption.[50,92] Power consumption for mechanical comminution can be controlled by adjusting the sizes of the initial input and desired final substrate, but will nonetheless impact the sustainability aspect of the overall process. In addition, the material's woody characteristics and moisture content also influence the required power input for this pre-treatment method.[46,109,112] Microwave irradiation applying electromagnetic fields for internal heating has also been investigated.[99,116] In bio-EtOH production, this approach is useful to selectively heat the polar bonds of the starting materials by vibrating the structure until the material is internally heated. As a result, complex lignocellulosic structures are fractured and made available for subsequent hydrolysis and fermentation.

Physiochemical methods, such as steam explosion, is another category of frequently employed pre-treatment process.[43,109,110,112] Steam explosion applies a combination of hydrothermal and sudden pressure changes to convert the biomass. This method is categorized under physicochemical pre-treatment for its fused mechanical- and chemical-driven characteristics. The steam strikes the biomass causing fiber separation and physically shortening of the fibers. In terms of chemical changes, auto-hydrolysis of acetyl groups that exist in hemicellulose takes place under high temperature, forming acetic acid, and an acidic environment can be initiated when the water is treated at high temperature. For this nature, steam explosion is more beneficial on hemicellulose-rich biomass. However, formation of inhibitors as the by-product of the steam explosion method is one major challenge that may disturb the microbial activity during the subsequent fermentation step.

*2.1.2.2. Saccharification through Hydrolysis.* After the pre-treatment of lignocellulosic starting materials, a hydrolysis process is usually required for the separation of long carbohydrate chains from cellulose or starch. This saccharification through hydrolysis is typically catalyzed by an enzyme or an acid. This stage is critical in bio-EtOH production since the quality of the hydrolysate will affect the subsequent fermentation process,[50,67] as yeast used in the fermentation process cannot utilize polysaccharides as a substrate for bio-EtOH production.[75,82,124] Acid hydrolysis benefits from the low cost of chemicals and the efficient process of chemical reactions.[47,57,82] However, the production of undesirable by-products that inhibit yeast growth in the following fermentation process and the requirement for acid recovery makes this method less favorable. Enzymatic hydrolysis is typically economically challenging due to the high cost of enzymes and is therefore often considered impractical for commercial purposes.[57,72,81,82,116] However, in comparison with acid hydrolysis, enzymes work under milder conditions with simple processes, which requires less equipment maintenance cost. Moreover, enzymatic hydrolysis essentially is a biological process, thus implying the sustainability of this process. The use of different enzymes in the hydrolysis process has been thoroughly reviewed in existing works.[50,57,72,81,82,116]

*2.1.2.3. Fermentation.* During the fermentation process, sugars are converted into bio-EtOH *via* the metabolic processes of microorganisms, such as bacteria and yeasts.[55,81,102,104,124] Monosaccharides (e.g., glucose and fructose) or disaccharides (e.g., maltose and sucrose) can be metabolized without oxygen and produce bio-EtOH and $CO_2$. For starchy hydrolysates, only glucose is present for the fermentation, presenting a simple substrate. However, different pentose and hexose sugars are present in hydrolysates of

### Table 2. Examples of Catalyst for the Dehydration of Bioethanol to Ethylene

| | Catalyst | Ethanol conversion (%) | Reaction temperature (°C) | Catalyst stability | Ref. |
|---|---|---|---|---|---|
| Acid catalysts | Phosphoric acid | 61−100 | 50−275 | Low | 128 |
| | Phosphotungsic acids | 75 | 180−150 | Low | 129 |
| | Silicoutungsic acids | 52 | | Stable | |
| | Phosphomolybdic acids | 11 | | Low | |
| | Phosphotungsic acids modified with cations | 100 | 190−260 | High | 128, 129 |
| | Silica supported heteropoly acids | 99.8 | 60−100 | High | 127, 131 |
| Molecular-sieve based catalysts | HZSM-5 modified with La and P | 100 | 240−280 | High | 132 |
| | Spherical catalyst with $\gamma$-$Al_2O_3$ | 99.5−100 | 350−450 | High | 133 |
| | ZSM-5 modified with Zn and Mg | 99.0 | 400 | Stable | 134 |
| | Zeolite ZSM-5 | 99.0 | 400 | Low | 125, 130 |
| | Zeolite HZSM-5 | 96.0 | 400 | Low | 135, 136 |
| | Silicoaluminophosphate (SAPO)-34 | 90 | 220−320 | High | 137, 138 |
| | H-ZSM-5/$H_3PO_4$ | 99 | 400−450 | Stable | 139 |
| | H-ZSM-5/SiC | 40−75 | 400 | High | 135 |
| Oxide catalysts | $\gamma$-$Al_2O_3$ | 99.0 | 350−450 | Stable | 140−142 |
| | $Al_2O_3$-MgO/syndol | 97.0−99.0 | 450 | High | 143 |
| | Transition metal oxide | 42.0−99.6 | 200-500 | High | 126 |
| | $Na_2O$-$Mn_2O_3$/$Al_2O_3$ | 92 | 300 | High | 144 |

biomass and natural microorganisms cannot typically ferment pentose sugars, although different strains of yeast have been reported to ferment xylose and arabinose.[50,75,85,102] Thus, a co-culture system is often employed in the fermentation of hydrolysates from lignocellulosic biomass.

Generally, five fermentation strategies can be applied for bioethanol production.[50] A first strategy is cell recycling batch fermentation, a process in which the main objective is to adapt yeast to become inhibitors. This process increases yeast performance as it can shorten reaction time and decrease minor carbon deviation for cell production. Another strategy is the SSF method.[85,99,102] In this process enzymatic hydrolysis and fermentation steps are applied together to obtain fermentable sugar to produce bio-EtOH. SSF has often been reported to increase the yield of bio-EtOH production, although the different ideal temperatures of the enzyme and the yeast can result in poor performance. A third strategy is separated hydrolysis fermentation (SHF), where hydrolysis and fermentation are conducted separately to produce bio-EtOH.[48,61,85,95,99,102] Semi-simultaneous saccharification and fermentation (SScF),[95,99,102] in which a short pre-hydrolytic step is applied before the SSF process presents a fourth fermentation strategy. Here, the bio-EtOH yield is typically slightly higher than with conventional SSF. Finally, consolidated bioprocessing (CBP) can be used for sugar fermentation, in which the decomposition of resistive biomass substrates into solubilized sugars is conducted alongside a metabolic intervention to guide the metabolic flow toward specific products with high yield.

The product of fermentation often is an azeotropic mixture of bio-EtOH and vinasse, making the separation of bio-EtOH another crucial part for obtaining high-purity bio-EtOH. Typically, this separation is done by distillation. The bio-EtOH obtained was typically distilled ethanol (93%), which is insufficient for subsequent processes that require high purity standards and may hence need to be subjected to additional purification.

*2.1.2.4. Dehydration.* Many different solid-catalysts have been reported as efficient for this process, including metal oxides, acidic zeolites, phosphoric acids, and heteropoly acids, as well as bio-catalysts,[125−129] as is summarized in Table 2.

The catalytical endothermic dehydration of bio-ethanol to bio-ethylene is the crucial step to eventually obtain the renewable polyolefin derivative. A representative catalytical synthesis of bio-ethylene from bio-ethanol was reported by Mao and co-workers in 1989,[130] where acidic ZSM-5 zeolite was employed as the catalyst. Only a dilute ethanol mixture, as low as 2%, could be used to produce ethylene.

The phosphoric acid catalyst was among the first catalysts to be used in the industrial synthesis of ethylene *via* catalytic ethanol dehydration.[128] The catalyst was prepared by impregnating clay or carbon with phosphoric acid. Ethylene obtained with this catalyst was of high purity, but the catalyst underwent rapid coking.[134,137] Hetero-polyacid catalysts are another kind of acid catalyst, which consist of strong, polybasic anionic complexes.[127,131] The possibility of employing various hetero-polyacids and their salts possessing Brønsted acidity in alcohol dehydration has been investigated in a number of studies.[129,131,134,137]

Catalysts based on molecular sieves have also been employed in the catalytical dehydration of bio-EtOH. Molecular sieves have a porous structure, unique acid−base properties, and a large specific surface area, making them widely employed as adsorbents and catalysts. Various types of zeolites as catalytic systems in the dehydration of alcohols to olefins have been reported,[23,125,136,140,145] including the use of natural zeolites and clays,[134] as well as bulk or supported synthetic zeolites such as NaX,[140] SAPO-34,[138] ZSM-5,[125] HZSM-5[146] and supported HZSM-5s.[135,136,139,145,147]

The molecular sieves that have been intensively studied in the hydrogenation of ethanol to ethylene are those based on silicoaluminophosphate (SAPO) and ZSM-5. Pure zeolite ZSM-5 was reported in the dehydration of a 20% ethanol solution to ethylene at 400 °C with a 99% ethanol conversion and ethylene selectivity up to 80%. On reducing the reaction temperature, the conversion and ethylene selectivity significantly decreased to 42% and 72%, respectively.[134] H-ZSM-5 zeolites were also studied for the dehydration of ethanol into ethylene, suggesting a direct single step method for ethanol conversion without a purification stage for obtaining high purity ethanol.[125,130] At an ethanol concentration of 15% and a temperature of 400 °C, the ethanol conversion and ethylene selectivity were 96% and 49%, respectively. Introduction of zinc and magnesium cations into the H-ZSM-5 catalyst was shown to enhance olefin selectivity, while similar effects are reported on H-ZSM-5 catalysts modified with phosphoric acid.[139]

Several different parameters have been studied regarding the stability and efficiency of HZSM-5 catalysts. For example, the addition of water to ethanol was reported to enhance the stability of the H-ZSM-5 catalyst and its ethylene selectivity.[146] Possible reasons for this include the reduced acidity of the catalytic sites in the presence of water and deactivation of the catalyst.[136,146] Thus, although considerable catalyst deactivation is observed in the presence of water, ethanol dehydration with zeolite catalysts is mainly performed with a large excess of water while it is recommended that the process should be conducted at elevated temperatures. Other modification methods such as changing crystallite size,[136] treating HZSM-5 with ion exchange to obtain the NKC-03A catalyst, and modifying ZSM-5 with lanthanum have also been reported.[132] Composite systems of zeolite catalysts were also reported with objectives to decrease the required reaction temperature and enhance the catalyst stability.[23,136,145] For example, a system employing titanium dioxide nanotubes as a deposition substrate of ZSM-5 catalysts has been reported,[134] whereby increasing the effective concentration of acid sites, ethanol conversion and ethylene yield were improved. Some drawbacks of zeolite catalysts include the rapid deactivation, their structural complexity and their high costs.[23,125,136,145]

Molecular sieves based on Si−Al phosphates, namely SAPOs, have been developed since 1984.[138] The ethylene dehydration properties of SAPO catalysts have been studied[138] and their stability has been screened relative to HZSM-5 and alumina catalysts, identifying SAPO-34 to have reasonable stability over 100 h of reaction. Under certain conditions, the activity of SAPO-34 in ethanol dehydration was reported to be higher than that of zeolite ZSM-5. The use of SAPO- and HZSM-based composite catalysts has also been studied,[134] with the composite catalysts system having increased acidity and catalytic activity at lower temperatures. The disadvantage of SAPO-type catalysts includes being quite expensive, considering the minor improvement in performance.

Metal oxides are another group of catalysts used frequently in the study of ethanol dehydration to ethylene. Examples of oxide catalysts include alumina,[141] magnesium oxide,[148] cobalt oxide,[148] chromium oxides[149] and transitional metal oxide catalysts.[126] Other mixed or supported systems have also been reported.[144,148,150,151] One representative example is aluminum oxides (alumina), which can serve as both a catalyst and support. This kind of catalysts was mainly used in commercial scale ethanol dehydration to ethylene.[133,134,141,152] The advantage of these catalysts is their improved stability compared to clay-based catalysts, but they originally suffered from producing low purity ethylene. The development of $\gamma$-$Al_2O_3$ catalyst has resolved this issue, showing a high ethanol conversion over 95% with ethylene selectivity over 96%.[134] Composite systems of alumina combined with silicon or silicon dioxide can enhance the stability, activity and selectivity of the catalyst.[145] Other modified systems such as syndol,[134] iron oxide[153] or zirconium oxide[134] composites were also reported as more active systems in ethanol dehydration compared to individual alumina. However, excessive acid sites in composite alumina catalyst systems result in undesired catalytic properties. It was also demonstrated that modifying alumina with chlorine ions can result in a considerable increase in the number of weak electron-acceptor sites, which enhances the catalyst activity. Apart from doping the catalyst system with other elements, increasing the specific surface area can also improve the performance of alumina catalysts. For example, mesoporous alumina catalysts with 1-20 nm pore sizes can exhibit an ethanol conversion of 99% and an ethylene selectivity of 98%.[152] Additionally, the granule shape and pore structure of alumina catalysts has also been demonstrated to affect the catalytic properties.[133]

In industrial ethanol dehydration units, individual alumina catalysts have been most employed due to the high-performance stability of the catalyst along with the high ethanol feed concentration that can be tolerated. More recently, modified oxide catalysts or composite catalytic systems have enabled improvement in outputs like ethylene selectivity and ethanol conversion.[23,143,148−150] However, for the sustainable production of bio-ethylene, the energy and economic cost of the preparation of catalysts also needs to be taken into account. Thus, only relatively straightforward techniques such as thermal activation of alumina catalysts seems promising for industrial use at this stage[134] and the development of cost-efficient methods of modifying alumina catalysts or designing composite catalytic system could be rewarding in the field of catalytic ethanol dehydration.

**2.1.3. Polymerization of Bio-ethylene.** Although numerous examples have been reported on the production of bio-ethanol from renewable feedstock and its catalytical dehydration into ethylene,[32−34,36,48] very few specifically demonstrated the subsequent polymerization of bio-ethylene into bio-polyethylene.[125,130] Most studies focused on the application of bio-polyethylene as the matrix to produce renewable composites with fillers such as natural fibers[154,155] and clays.[156] For example, bio-based composites of bio-ethylene and thermo-mechanical pulp corn stover fibers have been reported.[155] After the creation of a fiber-matrix interface *via* the addition of a coupling agent, the tensile strength of the composites increased over 100% for a 40 wt % reinforcement, when compared to unreinforced bio-polyethylene. The composites with other renewable polymers or fillers are often referred to as bio-composites.

Although commercialized renewable polyethylene has been used in markets,[157−159] the cost-efficiency of bio-polyethylene is still low compared to petrochemically derived polyethylene. Thus, the improvement of the cost-efficiency and the development of novel treatment procedures to produce bio-ethylene from bio-ethanol is deemed crucial for renewable polyethylene-based commodity plastics production. Alternatively, instead of preparing bio-polyethylene from previously described methods, the development of polyethylene-like materials whereby degradable linkers are introduced into the polyolefin backbone has received significant attention.[29,30,160,161] While such materials currently possess promising degradability, and hence chemical recyclability, their properties often differentiate too much from those of polyethylene in order to present a scalable alternative.

## 2.2. Propylene

Compared to the reported production of renewable polyethylene, the synthesis of bio-polypropylene remains rather

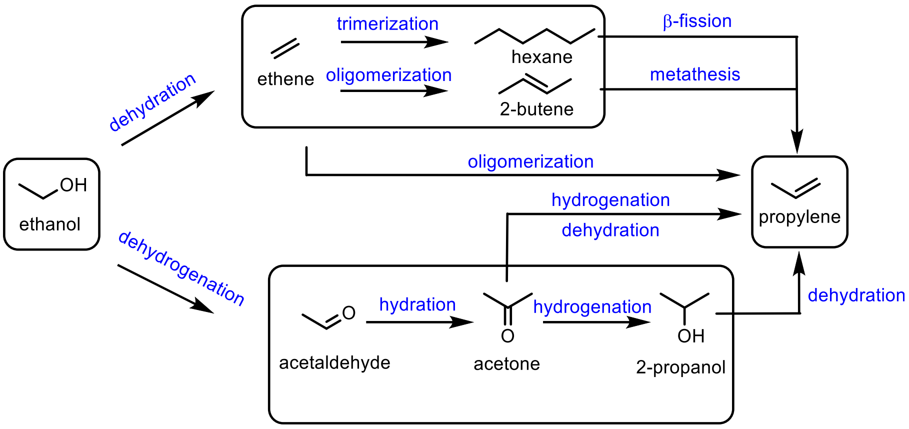


**Figure 3.** Possible pathways of production of propylene from ethanol.

limited.[21,162−165] While propylene is conventionally obtained from the steam cracking of crude oil, a very recent review[162] addressed the potential approaches for producing bio-polypropylene through the catalytic conversion of methanol or ethanol to propylene. Considering the wealth of research on bio-EtOH production previously mentioned and existing reports on bio-methanol (bio-MeOH) production, methanol-to-propylene (MTP) and ethanol-to-propylene (ETP) conversions have potential to serve as sustainable routes of bio-propylene.[162,163,166] In the MTP process, propylene is mostly produced as a by-product, with over 80% of ethylene as the major product.[162,165] However, as Koempel *et al.* reported, the production of olefin mixtures with predominantly propylene could be achieved *via* a catalytical MTP process.[163] Catalytic pyrolysis of biomass presents another potential route for producing bio-propylene, as the pyrolysis of biomasses results in a complex mixture that contains propylene.[23,28,167] The pyrolysis of biomass is a two-step process which contains fast pyrolysis and pyrolysis vapor conversion, for which catalysts such as ZSM-5 and calcium oxide have been studied.[28,167] The bio-ethanol dehydration, dimerization and metathesis procedure towards bio-propylene is the most researched approach, but additional pathways have been investigated (Figure 3). Different catalysts have been utilized in the ethanol dehydration process, with reported propylene yields ranging from 2% to 32%.[162] The use of a vast amount (>120 examples) catalysts for bio-propylene production has been reviewed in an excellent report elsewhere,[162] where factors impacting the propylene yield, such as the addition of metals and non-metals, are discussed in detail. Reaction conditions influencing the reaction efficiency include temperature, pH, water content present in the ethanol mixture, pressure, and the modification of catalysts with metal additives, non-metal additives, varied particle size, and varied component ratio. As mentioned earlier, the high cost of zeolite catalysts forms a concern in view of the commercial valorization of the ETP process. Considering the low yield of propylene as a major product, other procedures or catalysts that increases propylene selectivity could of interest to promote the renewable production of bio-propylene. Furthermore, no reports on the use of bio-propylene as monomer feed to synthesize polypropylene appear to be available to date.

## 2.3. Butylene

The renewable production of other olefins such as butylene is also rather undeveloped as compared to the production of bio-ethylene. Nonetheless, few reports are available on the production of bio-butylene *via* different methods, including the catalytical dehydration of butanol, the by-production from biomass and the conversion of ethanol (Figure 4).[103,147,168−172] However, butene is mostly obtained as a mixture of different isomers in these examples. Perhaps most notable is the highest selective (i.e., 99%) synthesis toward butene through the catalytic conversion of ethanol using designated metal doped oxide catalysts.[172] Different zeolite and zirconia-based catalysts have also been investigated, giving mixtures of 1-butene, *cis*/*trans*-2-butene and dibutyl ether from the catalytical dehydration of 1-butanol, while the highest selectivity toward 1-butene was reported to be 40%.[147] Evidently, the purification of butene isomer mixtures prior to its subsequent polymerization is an important challenge that needs to be addressed for the large scale production of butene monomers from renewable sources.

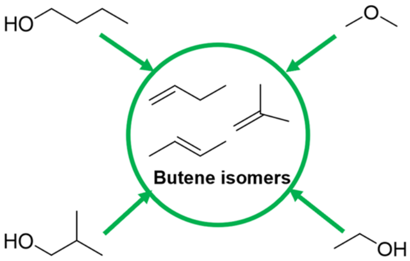


**Figure 4.** Various reported starting materials to produce butene isomers.

Aside from the plain olefin polymers, the sustainable preparation of other important polyolefins from bio-based sources is still in its infancy. For example, poly(vinyl chloride) (PVC) is the third most widely produced synthetic polymer, though a sustainable preparation of the vinyl chloride monomer is yet to be reported.

## 2.4. Styrene

First isolated in the 1830s, styrene is an aromatic monomer that is widely used in the production of polystyrene, polyesters, protective coatings, resins and rubbers.[173] The global production of styrene in 2017 was 15 million tons, with a market value of $43.1 billion.[173] Styrene is produced industrially through the dehydrogenation of ethylbenzene, which in turn is derived from crude oil.[173,174] Furthermore, dehydrogenation of ethylbenzene is a very energy intensive process, often requiring temperatures of 500−600 °C. In

**Table 3. Different Catalytic Systems for the Formation Styrene from Biobased Ethylbenzene**

| Entry | Catalyst | Temperature (°C) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|
| **1** | $Al_2O_3$ | 600 | 62 | 92 | 57 | 191 |
| **2** | 0.8 V/OMA | 550 | 52 | >97 | 50 | 192 |
| **3** | $V/TiO_2$-$Al_2O_3$ | 550 | 65 | 96 | 62 | 193 |
| **4** | $V_2O_5$/HMS | 600 | 73 | 99 | 72 | 194 |
| **5** | $MnO_2$-$ZrO_2$ | 650 | 74 | 98 | 72 | 195 |
| **6** | $Na/TiO_2$-$ZrO_2$ | 600 | 72 | 97 | 70 | 186 |
| **7** | $K_2O/TiO_2$-$ZrO_2$ | 660 | 72 | 98 | 71 | 196 |
| **8** | $MoO_3/TiO_2$-$Al_2O_3$ | 650 | 77 | 97 | 75 | 197 |
| **9** | $Co_3O_4/MgAl_2O_4$ | 600 | 82 | 98 | 80 | 198 |
| **10** | $CeO_2/ZrO_2$/SBA-15 | 650 | 67 | 93 | 62 | 199 |
| **11** | Carbon molecular sieve | 330 | 80 | 90 | 72 | 200 |
| **12** | Carbon nanotube 3 | 450 | 28 | 68 | 19 | 201 |
| **13** | Carbon multiwalled nanotube | 400 | 47 | 91 | 43 | 202 |
| **14** | Nanodiamond | 450 | 40 | 92 | 37 | 203 |

addition, the oxidative dehydrogenation of ethylbenzene is less intensive than simple dehydrogenation, and the various catalysts used in the oxidative dehydrogenation of bio-based ethylbenzene will be described. Hence, interests in a more sustainable production of ethylbenzene are highly desired.

Apart from bio-sourced ethylbenzene, a process focusing on the metathesis of cinnamic acid and cinnamate esters to produce styrene and acrylic acid/alkyl acrylates, called ethenolysis, will be highlighted as a different method for production of styrene. Also, the production of functional styrenics from bio-based chemicals such as cinnamic acids, ferulic acid, sinapic acid, coumaric acid and vanillin will be explored in this section. Apart from chemically alternative routes, styrene production through biochemical processes from phenylalanine using *Escherichia coli* will also be discussed.

### 2.4.1. Styrene from Biobased Ethylbenzene.

*2.4.1.1. Formation of Ethylbenzene from Lignin.* One way to increase the sustainability of styrene is to obtain the ethylbenzene starting material from biomass instead of petrochemicals. Lignin is an abundant and renewable source of biomass and the highly aromatic nature of lignin gives rise to its potential use in the production of aromatic chemicals.[175,176] Furthermore, ethylbenzene can be produced from the catalytic thermal degradation of lignin.[177] Li and co-workers produced ethylbenzene from lignin *via* a two-step process.[178] The first step was the depolymerization of lignin over a Re-Y/HZSM-5(25) catalyst. The major product of the depolymerization was benzene, and while at lower temperatures (i.e., 500 °C) the selectivity of benzene (measured in carbon-mol %) was poor (i.e., 26 C-mol %), it increased significantly to 90 C-mol % when the reaction temperature was increased to 650 °C. The resulting aromatic products were eventually reacted with ethanol over the catalyst HZSM-5(25) to form ethylbenzene. This reaction is reported to have occurred in two stages, the first being the dehydration of ethanol, producing ethylene and water, while the second step is the ethylation of benzene. While increasing the ratio of ethanol in the reaction increased benzene conversion, it also decreased the product selectivity. For example, when the feed to ethanol ratio was 2:1, the benzene conversion was 41% and the ethybenzene selectivity was 72 C-mol %. When the ratio was 1:2, the conversion of benzene increased to 68% but the product selectivity was only 43%. Production of ethylbenzene *via* this method has the advantage of using bio-based lignin and ethanol, which can be derived from sustainable sources. However, high temperatures are required for the depolymerization of lignin to proceed with high selectivity and there are also selectivity issues for the ethylation of benzene, which currently limit its sustainability.

Other studies have focused on screening different catalysts for the production of aromatics from lignin.[179−181] Wang and co-workers investigated Zn and Ga loaded catalysts, and obtained an optimum hydrocarbon aromatic yield of 37 wt % and a BTEX (benzene, toluene, ethylbenzene and xylene) selectivity of 62 wt %.[181] A different approach was explored by Luo and co-workers, investigating the formation of ethylbenzene from lignin.[180] The first step was the hydrodeoxygenation of lignin to form C3−C7 alkanes (20%), C8 ethylcyclohexane (42%) and cyclic C9−C17 alkanes (38%). A nickel/silicalite-1 catalyst was used with a reaction temperature of 300 °C and a hydrogen pressure of 6 MPa. The ethylcyclohexane was separated *via* distillation before dehydrogenation over a Pt-Sn/$Al_2O_3$ catalyst at 500 °C and 0.5 MPa $H_2$ resulted in a 99% yield of ethylbenzene. Separately, a modified $FeO_x$ $Ru/Nb_2O_5$ catalyst has also been used for the selective production of ethylbenzene from birch oil lignin through a dehydrogenative decarbonylation and hydrogenation process, obtaining a 63% selectivity.[179] While these methods require lower temperatures than for the depolymerization of lignin, harsh temperatures and metal catalysts are still required to achieve high yields, thus limiting the sustainability of these processes.

*2.4.1.2. Conversion of Ethylbenzene into Styrene.* The ethylbenzene obtained from biomass can then be dehydrogenated to produce styrene. The dehydrogenation of ethylbenzene requires high operating temperatures of 500−600 °C, which decreases the selectivity of the reaction.[182] In comparison, the oxidative dehydrogenation is exothermic and has a more favorable equilibrium. The reaction has been carried out previously using mild oxidizing agents such as $O_2$, $SO_2$ and $CO_2$.[173,183,184] Sugino and co-workers used $CO_2$ as a mild oxidizing agent, having the advantage of consuming a greenhouse gas, which increases the overall environmentally friendly aspect of this process.[173,183,184] Using $CO_2$ also has several other advantages, as it is cheap and abundant, increases catalyst selectivity by poisoning non-selective sites in the catalyst, and improves the rate of reaction.[184−186] Oxidative dehydrogenation proceeds through two steps whereby $H_2$ is produced in the first dehydrogenation step and then reacts with $CO_2$ to form water and carbon monoxide in a reverse water gas shift reaction.[173,187,188] The activation of $CO_2$ onto catalyst surfaces is an important step in the oxidative dehydrogenation reaction. While catalysts can activate $CO_2$ themselves, activators such as alkali or alkaline metals can be used.[183,189,190] Many different catalysts have been explored, including catalysts based on vanadium, mixed metal oxides and nanocarbon structures (Table 3).[173]

Vanadium catalysts have been heavily investigated for use in oxidative dehydrogenation reactions.[192,204] Vanadium catalysts were of particular significance because the V−O bond is effective at interacting with the alkyl protons, from the ethyl group of ethylbenzene, assisting in their abstraction. While vanadium and chromium oxides supported on alumina showed similar results to bare alumina (Table 3, entry 1), vanadium oxides on other supports have shown increased catalytic performance. For example, Li and co-workers compared vanadium catalysts supported on ordered mesoporous alumina (OMA) (Table 3, entry 2) and $\gamma$-alumina.[192] The OMA support showed a styrene selectivity of >97% and a stable conversion of 52% from ethylbenzene was obtained for 12 h. In contrast, a catalyst with the same loading of vanadium on a $\gamma$-alumina support showed a high ethylbenzene conversion in the first 2 h before significant deactivation took place. The results suggested that the support plays an important part in stabilizing the vanadium catalyst. Furthermore, OMA is more effective than y-alumina at stabilizing the active $V^{5+}$, while also suppressing its reduction to the less active $V^{3+}$ form due to the stronger interaction between OMA and the catalyst compared to $\gamma$-alumina. A hybrid $TiO_2$−$Al_2O_3$ support was used to obtain a styrene yield of 62% (Table 3, entry 3).[193] The hybrid support was effective at overcoming the limiting surface area of the active $TiO_2$ by combining it with the higher surface area $Al_2O_3$. The best support was shown to be hexagonal mesoporous silica (HMS).[194] At an optimum catalyst loading of 20 wt %, a maximum conversion of 73% and selectivity of 99% were achieved (Table 3, entry 4). The $V_2O_5$ catalysts supported on HMS were the most selective vanadium-based catalyst, and this can be attributed to the high surface area and the unique sponge-like particle texture of the support, which favors its application in heterogenous catalysis.[205] However, it is noteworthy that the synthesis of HMS supports has been reported to be energy intensive and time consuming, potentially limiting the potential of this catalytic system.[194]

Mixed metal oxide catalysts have also been effective for the oxidative dehydrogenation reaction of ethylbenzene, offering several advantages including stabilized conversions, selectivity, and reduced coke formation.[206] There are many examples of different mixed metal oxide catalysts that have been used to obtain high conversions and styrene selectivity (Table 3, entries 5−10).[186,195−199] Of those, molybdenum oxide- and cobalt oxide-based catalysts resulted in the best styrene yields of 75% and 80%, respectively.[197,198] Nagaraja and co-workers developed a $MoO_3/TiO_2$-$Al_2O_3$ catalyst that achieved a conversion of 77% and styrene selectivity of 97% after 1 h of reaction at 650 °C, with an optimum molybdenum loading of 7.5 wt % (Table 3, entry 8).[197] Further doping with molybdenum decreased the ethylbenzene conversion and the catalyst deactivated over time, with the conversion and selectivity falling to 50% and 85% after 40 h, respectively. The performance of this catalyst was attributed to the high surface area and the active $Mo^{6+}$ species being effectively stabilized by the $TiO_2$−$Al_2O_3$ support. Rao and co-workers developed a $Co_3O_4/MgAl_2O_4$ catalyst that achieved an even higher styrene yield of 80% (Table 3, entry 9).[198] The higher yield was attributed to the synergistic interface between the active catalyst and support leading to an increased active surface. The importance of the interaction with the support was shown by a significant decrease in the conversion when MgO and $\gamma$-$Al_2O_3$ supports were doped with $Co_3O_4$.

One of the major disadvantages of the reported catalytic systems is their deactivation due to coke formation or catalyst reduction. Coke formation has been attributed to several side reactions, including ethylbenzene cracking and styrene oligomerization reactions.[207] When a $\gamma$-alumina support was used, deactivation of the catalyst was observed due to coke formation.[191] This deactivation was limited by adding a thin carbon layer, with an optimum loading of 18.6 wt %.[208] A higher wt % reduced the styrene selectivity and ethylbenzene conversion, as it changed the textural properties of the catalysts. Again, the nature of the support was shown to have an impact on catalyst deactivation. For example, deactivation is more severe for $\gamma$-alumina because of its smaller surface area, pore volume and pore diameter causing them to become blocked by coke deposition more easily, when compared to the ordered mesoporous alumina.[192] Reduction of the catalyst also leads to catalytic deactivation. In the oxidative dehydrogenation process, the released hydrogen from ethylbenzene reacts with lattice oxygen to release water, leading to a reduction of the catalyst activity. Carbon dioxide plays an important role in removing the hydrogen through the reverse water gas shift reaction. It has been reported that $CeO_2$ is better at protecting the lattice oxygen than $Fe_2O_3$ and $V_2O_5$, consequently reduction of the catalyst is limited.[209] The $CeO_2$ doped catalyst was found to improve the acid−base properties of the catalyst, which are important for catalysis. Burri *et al.* developed a 25/25CZS catalyst (containing $CeO_2$, $ZrO_2$ and 75 wt % of a SBA-15 support) for the oxidative dehydrogenation of ethylbenzene, obtaining a styrene yield of 62% after 5 h (Table 3, entry 10).[199] The high activity of the catalyst was attributed to the active $CeO_2$−$ZrO_2$ catalyst being dispersed on a high-surface-area support. The styrene selectivity remained around 93% during the 10 h reaction time, while the conversion fell slightly to 64%, indicating good catalyst stability.

Cheaper alternatives to metal oxide catalysts have been sought for styrene production, such as graphene, carbon nanotubes or nano-diamond (Table 3, entries 11−14).[173,189,210,211] As well as being less expensive, these carbon-based catalysts also offer other advantages when compared to metal-based catalysts. For example, ultra-high-surface-area molecular sieves have been used as catalysts (AX-21) for the oxidative dehydrogenation of ethylbenzene, obtaining a conversion of 80% and a styrene selectivity of 90% (Table 3, entry 11).[200] While the selectivity of this catalyst is lower than the majority of metal-based catalysts, there are two advantages to AX-21. First, the conversion of ethylbenzene is very high (i.e., 80%) compared to when metal-based catalysts were used. Second, a significantly lower reaction temperature had to be used when using AX-21 (i.e., 330 °C) compared to temperatures >550 °C that were required when using metal-based catalysts. The high activity of AX-21 was accredited to the high surface area of the catalyst, which was reported to be 3000 $m^2$ $g^{-1}$. As well as molecular sieves, carbon nanotubes have also been used as non-metallic catalysts for styrene production from ethylbenzene.[201] Nonetheless, carbon nanotubes require an oxidative pre-treatment which improves their conversion potential from 20% to 28%.

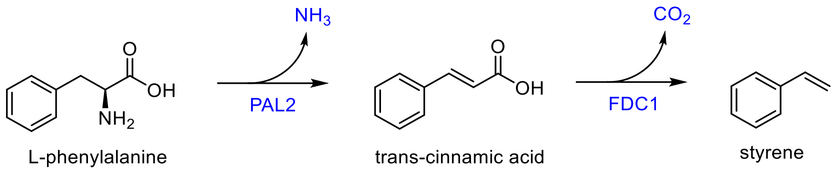


**Figure 5.** Synthesis of styrene from L-phenylalanine *via* a biochemical approach.

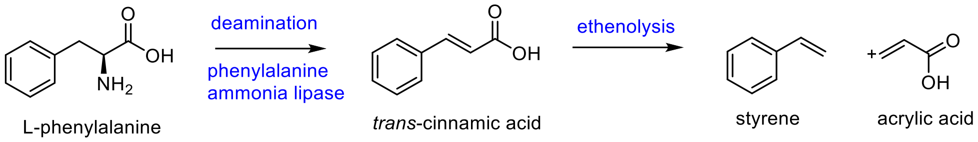


**Figure 6.** Two-step synthesis of styrene and acrylic acid from phenylalanine *via* deamination and ethenolysis.

This highlights the importance of oxygenated groups on the catalyst surface. However, carbon nanotubes proved not as effective as activated carbon (42% styrene yield) and metal-based catalysts (50−80% styrene yield).

Oxidative treatments are used to introduce oxygenated functional groups, for example, carboxylic, carbonyl and hydroxyl groups, at the surface of carbon nanotubes.[212,213] These treatments can include gas phase oxidation, using a range of oxidants including air, steam or a mixture of $Cl_2$, HCl and $H_2O$.[212,214−216] Liquid phase oxidation involves the use of oxidizing agents such as $HNO_3$, $H_2O_2$, $KMnO_4$ or a mixture of $H_2SO_4$, $HNO_3$, $KMnO_4$ and NaOH.[212,217−219] However, using strong acids and oxidants can destroy the carbon nanotube structure, hence why the milder nitric acid is the most common oxidizing agent used in these treatments.[212] When multiwalled carbon nanotubes were subjected to an oxidative pre-treatment utilizing UV light and $H_2O_2$, an ethylbenzene conversion of 47% and a styrene selectivity of 91% was obtained (Table 3, entry 13). Temperature was also shown to effect catalytic performance due to a decrease in the number of oxygenated groups as the temperature was increased from 700 to 3000 °C.[220] This correlated with a decrease in catalytic activity as shown by a decrease in conversion from 50% to less than 3% for temperatures of 700 and 3000 °C, respectively.

Nanodiamonds are a less frequently studied class of carbon nanomaterial and have unique characteristics and properties, including a unique $sp^3/sp^2$ structure, high thermal and chemical stability and a high surface area.[221] Nanodiamond catalysts were reported to be more active and selective than other forms of carbon catalysts including carbon nanotubes and activated carbon.[222] The increase in activity originates from the $sp^3/sp^2$ structure giving rise to a variety of different defects and surface functional groups. These carbon nanodiamonds have been combined with carbon nitride to obtain catalysts that demonstrated 99% styrene selectivity.[223] Nanodiamonds can be used to combine both dehydrogenation and oxidative dehydrogenation, demonstrating an ethylbenzene conversion of 40% and 92% styrene selectivity in oxygen-lean conditions (Table 3, entry 14).[203] Furthermore, the $sp^3/sp^2$ structure remained intact and active ketone functionalities were regenerated *in situ*. The oxygen-lean conditions gave a superior ethylbenzene conversion than direct dehydrogenation (5.5%), while the selectivity was slightly lower than for the direct dehydrogenation (i.e., 98%). Adding more oxygen increased the activity of the catalyst, as more oxygenated functional surface active groups were present, but this also led to a decrease in selectivity and catalyst stability. Finally, carbon nanotubes and nanodiamonds have been combined into a single catalytic system, demonstrating high styrene selectivity (i.e., 98%) but low ethylbenzene conversion (i.e., 18%).[224,225]

### 2.4.2. Biochemical Routes to Styrene.

Biochemical routes are important when considering sustainable reactions as they remove the need for metal catalysts and high operating temperatures.[226] Styrene has been produced by the fermentation of glucose using *E. coli*; however, the yield is limited by the toxicity of styrene toward *E. coli*, which is predicted to be around 300 mg $L^{-1}$.[227,228] The solubility of styrene in water is only 320 mg $L^{-1}$ at 32 °C, which is similar to fermentation conditions. Thus, optimizing conditions such that styrene can phase separate from the cultures would help to alleviate the associated toxicity problem.[227] Furthermore, if spontaneous phase separation could be achieved, the produced styrene would be high purity due to water being very insoluble in styrene.

McKenna and co-workers were the first to synthesize styrene from biomass using an engineered microbial platform in 2011.[229] The engineered *E. coli* was able to generate styrene with a titer of 0.26 g $L^{-1}$ by converting glucose into L-phenylalanine, *trans*-cinnamic acid and then styrene. Nevertheless, problems such as low enzyme activity and styrene toxicity were encountered. The titer could be improved to 0.35 g $L^{-1}$ when an *in situ* product removal approach was taken using isopropyl myristate as a solvent.[230] Using a solvent extraction method to reduce the impact of styrene toxicity with bis(2-ethylhexyl)phthalate generated a titer of 0.84 g $L^{-1}$.[231] The titer was increased further by Lee *et al.* who optimized the production of styrene by using *E. coli* YHP05 and the coenzyme ScFDC along with an *in situ* product recovery.[232] An optimum titer of 1.7 g $L^{-1}$ was obtained for the shake flask production, while when in a liter scale fed-batch reactor, a titer of 5.3 g $L^{-1}$ was achieved. Grubbe and co-workers produced two enzymes *in situ via* cell-free protein synthesis.[233] These two enzymes, phenylalanine ammonia lyase 2 (PAL2) and ferulic acid decarboxylase 1 (FDC1) were used to convert L-phenylalanine into styrene in a two-step synthesis with a titer of 4.2 g $L^{-1}$ (Figure 5). In the first step, PAL2 catalyzed the transformation of L-phenylaniline to *trans*-cinnamic acid through the loss of ammonia.[234−236] The *trans*-cinnamic acid then undergoes decarboxylation to form styrene, catalyzed by the FDC1 enzyme.

The biochemical production of styrene has many benefits including being less energy intensive, producing fewer toxic products and reducing greenhouse gas emissions. Nonetheless, the biochemical pathways to styrene cannot produce styrene

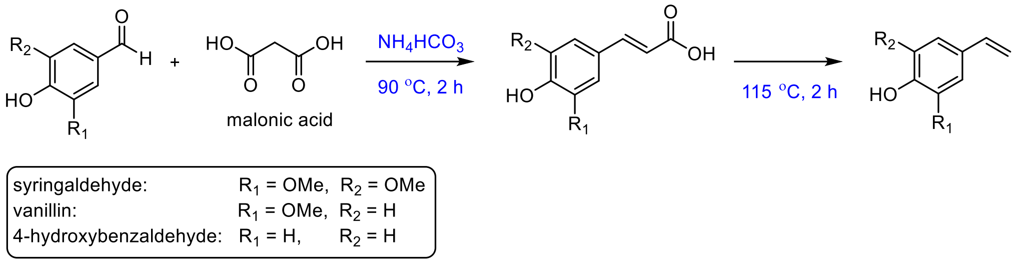


**Figure 7.** Synthetic route to produce 4-vinylphenol derivatives from syringaldehyde, vanillin and 4-hydroxybenzaldehyde.

**Table 4. Reaction Conditions and Results for the Two-Step Synthesis of 4-Vinylphenol Derivatives from Syringaldehyde, Vanillin and 4-Hydroxybenzaldehyde**

| | Step 1 | | | Step 2 | | | | |
|---|---|---|---|---|---|---|---|---|
| Substrate | Temperature (°C) | Reaction time (h) | Yield (%) | Temperature (°C) | Reaction time (h) | Yield (%) | Overall yield (%) | Ref. |
| **1a** | 90 | 2 | 93 | 115 | 2 | 98 | 91 | 241 |
| **1b** | 90 | 2 | 95 | 115 | 2 | 97 | 92 | 241 |
| **1c** | 90 | 2 | 94 | 115 | 2 | 96 | 90 | 241 |

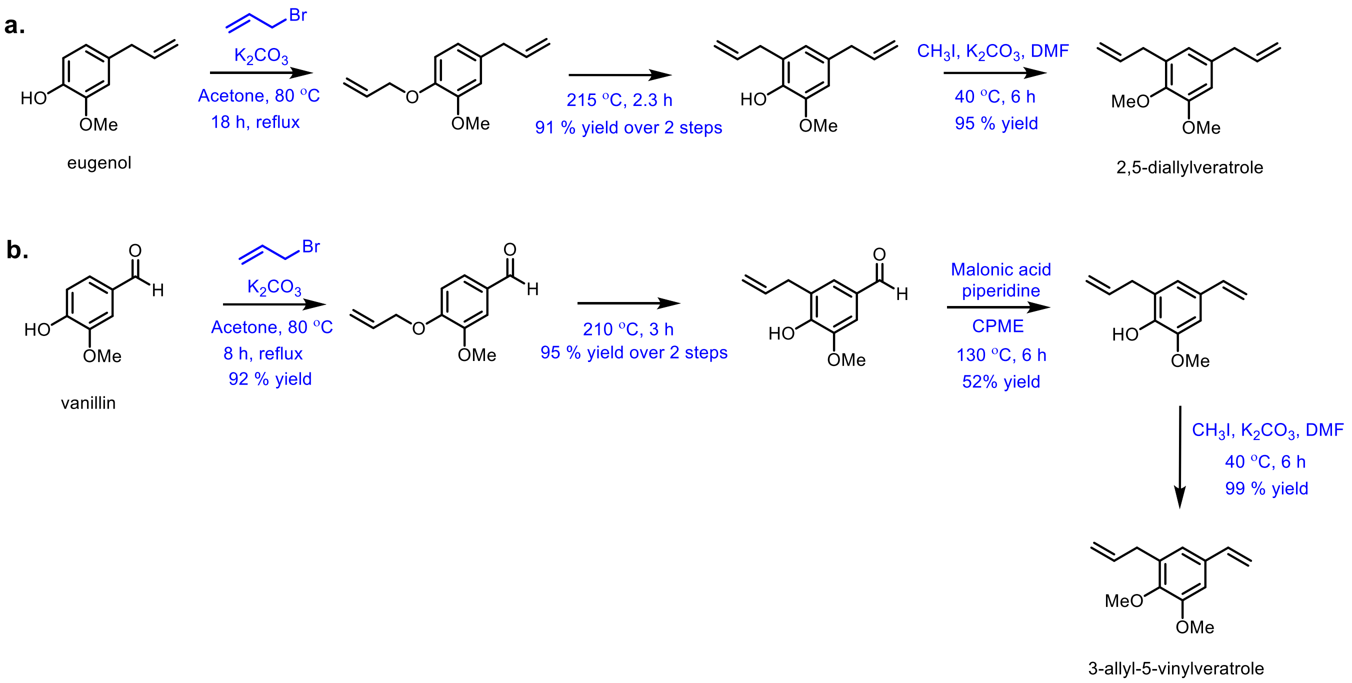


**Figure 8.** Multi-step synthesis of DV and AVV from eugenol and vanillin, respectively.

currently on a large enough scale to meet demand, meaning further research is required to become industrially viable.[237]

The *trans*-cinnamic acid produced *via* the biochemical reaction of L-phenylalanine with PAL2 can eventually be reacted in a metathesis reaction, called ethenolysis, with ethene to produce styrene. The products of this reaction are styrene and acrylic acid, two valuable vinyl monomers (Figure 6). Alkyl acrylates could also be produced when cinnamate esters were used instead of cinnamic acid.[236] For the ethenolysis of all substrates tested, the best catalyst was the Hoveyda−Grubbs second generation catalyst. This was attributed to the electron donating carbene ligand stabilizing the electron deficient double bond in the substrate. However, this reaction proceeded with limited yields. The styrene yield when cinnamic acid was used was 29%, while all the cinnamate esters tested obtained lower yields between 12 and 23%. This ethenolysis was more challenging than previous examples reported because of the double bond in the substrate being electron deficient.[236,238] In previous work, increasing the pressure of ethene generally led to an increase in the conversion; however, the reverse was true for this ethenolysis.[236,238,239] It was suggested that this was due to the double bond being electron deficient, and at high pressures ethene would predominantly undergo self-metathesis.[236] At lower pressures, there is less ethene in the system for this side reaction to take place, the cross metathesis with cinnamic acid/esters was favored.[236] However, the disadvantage of using lower ethene pressures is that the self-metathesis of styrene to form stilbene occurs at a faster rate. In an ethenolysis of styrene with 20 bar ethene the ratio of styrene to stilbene was 83:17 while at 1 bar pressure the selectivity fell to a ratio of 57:43.[236] This trend was attributed to a higher selectivity being achieved when a more reactive metathesis substrate is used in excess.[236,240] While ethenolysis has the advantage of producing

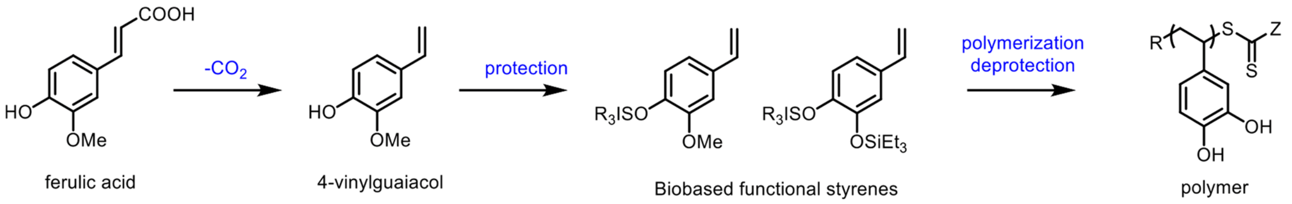


**Figure 9.** Synthesis, protection and polymerization of bio-based styrenics derived from ferulic acid.

two important monomers for the polymer industry, low yields and selectivity problems hinder its feasibility, while the use of ethene limits the sustainability aspect of this process unless it is also sustainably sourced.

**2.4.3. Functional Styrene Derivatives.** Biobased alternatives to styrene are of interest and a series of functional styrenics featuring phenolic and methoxy groups have been synthesized. While the synthesis of styrene requires very high operating temperatures, the synthesis of functional styrenics operates at significantly lower temperatures. Functional styrenics possess a similar structure to styrene and can thus mimic the properties of styrene. The structures of some of the bio-based starting chemicals, derived from lignin, used are displayed in Figure 7 and include syringaldehyde (**1a**, Table 4), vanillin (**1b**, Table 4) and 4-hydroxybenzaldehyde (**1c**, Table 4). Meuldijk and co-workers produced functionalized styrenics through a two-step synthesis as shown in Figure 7, while the key results are summarized in Table 4.[241] The first step of the synthesis was a green Knoevenagel reaction between the aldehyde functionality of the bio-reactants with malonic acid to form cinnamic acids, using ammonium hydrogen carbonate as a catalyst and a temperature of 90 °C. The next stage of the synthesis involved the decarboxylation of the $\alpha,\beta$-unsaturated carboxylic acids to form the 4-vinylphenol derivatives. High overall yields of 91%, 92% and 90% were obtained for substituted styrenics produced from syringaldehyde, vanillin and 4-hydroxybenzaldehyde, respectively. Acetylated versions of the monomers were also formed *via* reactions between the 4-vinylphenol monomers, acetic anhydride, and sodium acetate at 90 °C for 30 min. The acetylation proceeded with high yields (>98%) for all monomers. This process has the advantage of using lignin derived starting materials as well as the naturally occurring malonic acid. It is also noteworthy that the temperatures required for this reaction are significantly lower than to produce styrene from the dehydrogenation of ethylbenzene.

Eugenol is another bio-based aromatic chemical derived from lignin that can be used to synthesize functional styrene. For instance, Yu and co-workers synthesized two aromatic monomers featuring two double bonds, i.e., 2,5-diallylveratrole (DV) and 3-allyl-5-vinylveratrole (AVV).[242] The synthetic routes for both monomers from eugenol and vanillin respectively are illustrated in Figure 8. A three-step synthesis from eugenol resulted in the formation of 2,5-diallylveratrole. The first step was the allylation of eugenol with allyl bromide and potassium carbonate in acetone, followed by a distillation which resulted in an aromatic Claisen rearrangement. The yield of these two steps was 91%, with the final step being a methylation with potassium hydroxide and iodomethane in a yield of 95%. The second monomer, 3-allyl-5-vinylveratrole, was synthesized in a slightly adjusted synthetic route, using vanillin as the starting material instead of eugenol. The first two steps were the same as for the previous monomer and achieved an overall yield of 95%. An extra step compared to the eugenol synthesis was required to convert the aldehyde group of vanillin to a vinyl group and was completed using a Knoevenagal condensation with malonic acid and piperidine in cyclopentylmethyl ether. A lower yield of 52% was reported for this additional step before the final methylation step proceeded with a 99% yield. These monomers have been shown to successfully replace styrene as the reactive diluent in vinyl ester thermoset networks, hence producing (partially) bio-based thermosets.[242] The most promising result was replacing styrene with 3-allyl-5-vinylveratrole (>90% bio-based from this synthetic method), which matched the performance of styrene when formulated at 30 wt % of the diluents.

Youngblood and co-workers synthesized derivatives from 4-vinylguaiacol including 2-methoxy-4-vinylphenyl acetate and 2-methoxy-4-vinylphenyl oleate.[243] These resulting monomers were tested as potential styrene replacements in polyester thermoset networks. The protection of 4-vinylguaiacol was necessary, however, as phenolic compounds act as inhibitors in radical reactions.[243,244] Moreover, a general trend was observed in which increasing the fraction of the bio-based styrene incorporated into the polymer led to a detrimental impact on at least one of the properties investigated (i.e., mechanical, thermal and water-uptake properties). Another bio-monomer using different protecting groups, 2,3-dimethoxystyrene, outperformed the others; however, it did lead to problems such as fast gelation and low polyester solubility. Nevertheless, a 50:50 mix of bio-styrene to styrene resulted in polymers with equivalent physical properties to the plain styrene polymers. The use of silyl protecting groups further allowed the bio-styrene to be polymerized with conversions of >95% (Figure 9).[244] Similar polymerizations have been carried out for protected vinyl catechols, which were formed *via* a decarboxylation of caffeic acid followed by protection, with yields of 74−98% being achieved.[245,246] The protected monomers were shown to be successfully polymerized *via* anionic and several controlled radical polymerization techniques. The anionic polymerization of a TBDMS protected vinyl catechol achieved the greatest success with near-quantitative conversion (i.e., 99%), molecular weight of 14 100 Da and a polydispersity index of 1.04.[245]

Cinnamic acids are another class of substrate that can be conveniently converted into functional styrenics *via* both biochemical and chemical routes. Cinnamic acid can be converted into 4-hydroxystyrenes using enzymatic decarboxylation. Previous work demonstrated that steric hindrance is an important factor that can prevent binding to the enzyme.[247] This was shown, for instance, through *p*-coumaric acid having the highest rate of $CO_2$ evolution (91 $\mu$L in 30 min) compared to the more sterically hindered substrates, e.g., caffeic acid (68 $\mu$L in 30 min) and ferulic acid (26 $\mu$L in 30 min). More sterically hindered substrates such as sinapic acid and substrates without a 4-hydroxy group (e.g., cinnamic acid, *o*-

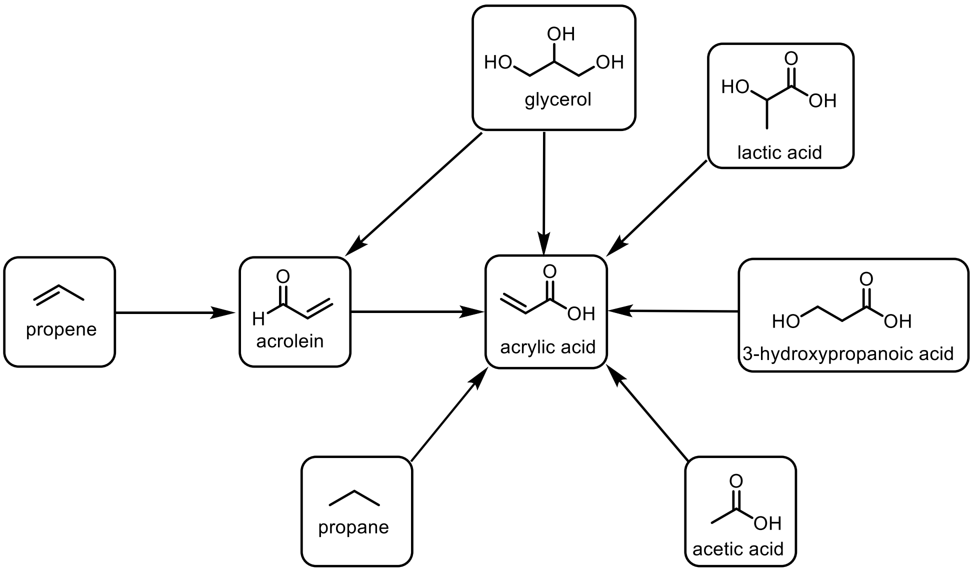


**Figure 10.** Synthetic routes to produce acrylic acid from various bio-sources including glycerol, lactic acid, 3-HPA and acetic acid.

and *m*-coumaric acids) showed no $CO_2$ evolution after 30 min.[247] The microwave heated base-catalyzed decarboxylation of different cinnamic acids has also been investigated.[248] As with the enzymatic route explored by Finkle, the 4-hydroxy position was vital for the reaction to proceed. In this case, there were two competing reactions, being the formation of bio-styrene and the formation of an amide. The optimized yields of styrene obtained from ferulic acid and *p*-coumaric acid were both 63% and proceeded with selectivity for only the bio-styrene. Other hydroxy-substitution patterns gave either lower yields of bio-styrene, or poor selectivity favoring the formation of the amide. Liu and co-workers used *N*-heterocyclic carbene precursors to catalyze the decarboxylation of cinnamic acids.[249] Once again, the substitution pattern was an important parameter in determining the success of the reaction with the highest yields being obtained for ferulic acid (100%), sinapic acid (100%) and caffeic acid (97%).

Cadot *et al.* synthesized bio-styrene in a one pot synthesis by heating different cinnamic acids with a $Cu(OH)_2$ catalyst and 1,10-phenanthroline ligand in a green solvent (i.e., PEG-6000).[250] A yield of 96% was obtained when ferulic acid was used while yields of between 31 and 73% were obtained for cinnamic acid, sinapic acid and *m*-coumaric acid. It was noted that decarboxylation of caffeic acid and *p*-coumaric acid were observed to be successful through observation of $CO_2$ evolution, but yields were unable to be obtained due to the immediate polymerization of the monomers. From a sustainable chemistry perspective, it is noteworthy that the copper catalyst was shown to be effective for four runs in the decarboxylation of ferulic acid, with a yield of 96% obtained on the fourth run.[246,250]

In summary, various routes from bio-based sources are available to produce bio-styrene, including chemical and biological pathways. Compared to the oxidative dehydrogenation of ethylbenzene, these routes have the advantage that they require significantly lower temperatures and do not require the same expensive heterogeneous catalysts. While each step may proceed with high yields, these synthetic routes often require multiple steps and this limits both the overall yield and the sustainability. However, these functionalized bio-styrene monomers show comparable properties and performance to standard styrene.

## 3. ACRYLICS

### 3.1. (Meth)acrylates

Acrylic and methacrylic monomers are widely used throughout the polymer industry. Acrylic acid and its esters were listed as the 25th top organic chemical product, and the market for acrylic acid grew from \$11 billion in 2013 to nearly \$19 billion in 2020.[173] Similarly, methacrylic acid and alkyl methacrylates are important monomers to form polymers such as PMMA, which are used in many applications such as coatings, paints and electronics.[173] The PMMA market was estimated at \$7 billion in 2018 and is anticipated to grow by 17% to ca. \$12 billion in 2022.[173] Currently, acrylic acid is produced through the oxidation of propane which is obtained from crude oil. Alkyl acrylates are then produced by the esterification of the acrylic acid with their corresponding alcohol. For methyl methacrylate, the majority of industrial production is carried out through the acetone-cyanohydrin process.[173,251] As well as having the problem of using petrochemical feedstocks, this process also produces large amounts of emissions of greenhouse gases, has poor selectivity and a poor atom economy.[252] There have been a vast number of studies into the production of acrylic and methacrylic monomers from biomass. For instance, acrylic acid has been derived from glycerol, lactic acid, 3-hydroxypropanoic acid and acetic acid.[173] The main focus of this section will be reviewing the different catalytic systems used to convert each of these bio-derived platform chemicals to acrylic acid. It is noteworthy, that acrylic acid and alkyl acrylates can be produced, as well as styrene, in ethenolysis (refer to section 2.4.2).[236]

For methacrylic acid, one potential approach is to replace petroleum-derived chemicals with their biomass-derived equivalents and use these in the current production methods. For example, for the acetone-cyanohydrin process, the fermentation of plants gives ethanol and acetone, which can be used in the process to form methacrylic acid.[252,253] However, producing the feedstock from biomass does not overcome other disadvantages of this process, such as low selectivity, low atom economy and the formation of toxic intermediates, including acetone cyanohydrin.[252] Hence, the main focus of this section is to explore the different catalytic systems which can convert bio-derived chemicals into methacrylic acid. The bio-sources discussed here are isobutane, produced through the thermo-catalytic process and fermentation of sugars, and bio-based carboxylic acids, such as itaconic and citric acids. Thus, bio-based approaches to form alkyl, cyclic and aromatic (meth)acrylates will be discussed.

For alkyl (meth)acrylates, the main focus herein is to highlight different production methods that involve glycerol, acrolein, acetic acid, alkyl lactates and vegetable oils/lipids. For the cyclic (meth)acrylates, terpenes, isosorbide, lactones and levoglucosenone are identified as key platform chemicals. Finally, aromatic (meth)acrylates will be evaluated where the majority of studies use lignin as the biomass. It is noteworthy that many of the thus far reported approaches are not fully bio-based as it involves coupling a bio-sourced platform chemical with a non-bio-derived reagent, such as methacrylic anhydride or (meth)acryloyl chloride. However, these approaches have been evaluated due to one of the major components of the reaction being sourced from biomass. Where more sustainable methods have been investigated, these have been discussed and their advantages and limitations have been highlighted.

#### 3.1.1. Acrylic Acid.

Acrylic acid is one of the most important industrial chemicals and its alkyl esters are widely used in products such as paints, coatings and adhesives.[254−256] Acrylic acid is produced from petrochemicals through the oxidation of propene.[254,256−258] Nonetheless, acrylic acid can be produced sustainably from bio-sources including glycerol, lactic acid, 3-HPA and acetic acid, as illustrated in Figure 10.[173,259−262]

##### *3.1.1.1. From Glycerol.*

The value of using glycerol has increased as it is a readily available bio-source due to its formation as a by-product in biodiesel production.[173,259,262] Acrylic acid can be synthesized from glycerol by either a two- or one-step process (Figure 11).[173,263] In one reported two-step synthesis, a double dehydration forms the intermediate acrolein, which then undergoes an oxidation to form acrylic acid. Another two-step pathway involved the dehydration of glycerol to allyl alcohol before an oxidation to acrylic acid. Alternatively, a single-step route can be applied, involving the dehydration to acrolein and oxidation of acrylic acid over a multifunctional catalyst.

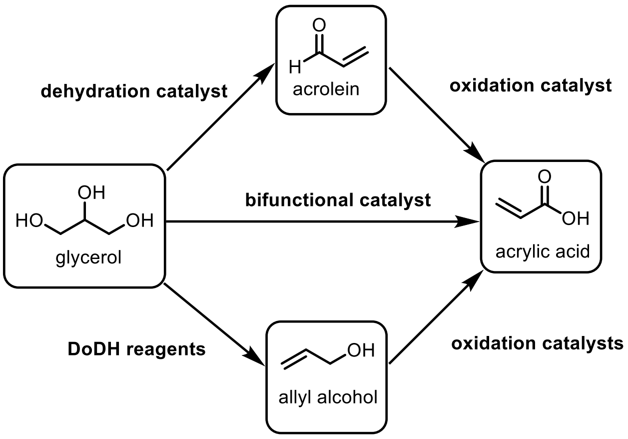


**Figure 11.** One-step and two-step routes to produce acrylic acid from glycerol.

There have been studies into many different catalysts for the production of acrylic acid from glycerol, including Keggin-type catalysts, metal mixed oxide-based catalysts and zeolite-based catalysts.[173,259] Catalysts containing vanadium have also been thoroughly studied as multifunctional catalysts for the one-step synthesis of acrylic acid from glycerol, with examples summarized in Table 5. The multifunctional catalyst allows for the dehydration of glycerol to acrolein and the subsequent oxidation into acrylic acid to proceed in one step. The vanadium presence in the catalysts enables the oxidation of acrolein into acrylic acid (Table 5, entry 1), while doping it with other metals (Table 5, entries 2−6) enables acrylic acid formation below 310 °C.[263−268] These catalysts could reach a conversion of >99%; however, acrylic acid selectivity is an issue, and this limits the yields (cf. Table 5). While the doped catalysts were able to function at lower temperatures, the highest yield of 57% was for the undoped vanadium Keggin-type catalyst, which operated at a temperature of 340 °C.[263] Doping with niobium proved to be more effective than doping with iron, molybdenum and tungsten, with a yield of 51% being achieved.[268] For the doped catalysts, increasing the temperature resulted in a decrease in selectivity, as the formation of heavy products was favored.[265]

The introduction of phosphoric acid into catalysts increased the acidity and improved the oxidation, while hindering the oxidation of acrylic acid to form $CO_x$ side products.[269] When doped with phosphoric acid, an acrylic acid selectivity of 59% was obtained, which was notably higher than for the metal doped catalysts (Table 5, entry 7).[269] A different type of catalyst consisting of copper nanocrystals supported on a $SiO_2$−$MnO_2$ support has also been developed.[270] This catalyst was the most selective for acrylic acid, with an optimum selectivity of 75%, but had a significantly lower glycerol conversion of only 77% (Table 5, entry 8). However, even with low conversion, an acrylic acid yield of 58% was comparable to the phosphoric acid doped catalyst and was significantly higher than most of the metal doped mixed metal oxide catalysts explored. Another advantage of using this catalyst was that a significantly lower temperature of 70 °C could be used. The reusability of the catalyst was also explored and after 4 cycles the glycerol conversion and acrylic acid selectivity had only fallen slightly to 73% and 72%, respectively.

Mixed metal oxides have been combined with zeolites to form catalysts for the oxidative dehydration of glycerol (Table 5, entries 9−11).[266,271,272] When the catalyst HZSM-5/MoVO was used, an acrylic acid selectivity of 47% was observed at full conversion.[266] In this case, a two-bed system was utilized by having a layer of an acid catalyst (i.e., HZSM-5) on a layer of MoVW-5. This system overcame the problem of glycerol oxidation by ensuring that all the glycerol had been converted on the first bed, before the subsequent oxidation of acrolein on the second bed takes place. A vanadium doped SiW/HZSM-5 catalyst achieved a lower acrylic acid yield of 36%.[271] However, an advantage of this catalyst was that it required a significantly lower temperature than the other mixed metal oxide/zeolite hybrid catalysts. It was noted that the textural properties of the catalysts are equally as important as the surface properties when considering the catalytic activity. A bi-functional H,Fe-MCM-22 catalytic system has also been developed with an optimum glycerol conversion and acrylic acid selectivity of 93% and 57% being obtained, respectively.[272] This catalyst had

**Table 5. Different Catalytic Systems for the Formation of Acrylic Acid from Glycerol**

| Entry | Catalyst | Temperature (°C) | Reaction time (h) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| **1** | $Cs(VO)_{0.2}(PMo)_{0.5}(PW)_{0.5}$ | 340 | 1 | 100 | 57 | 57 | 263 |
| **2** | W-V-Nb-O | 290 | nr | 100 | 34 | 34 | 265 |
| **3** | VWO | <310 | 2 | >99 | 26 | 26 | 264 |
| **4** | MoVW-5 | 250 | 14 | 100 | 31 | 31 | 266 |
| **5** | WMoV-3 | 290 | 70 | 100 | 40 | 40 | 267 |
| **6** | NbVWO | 265 | 37 | 100 | 51 | 51 | 268 |
| **7** | $PO_4/W_{2.2}V_{0.4}Nb_{2.4}O_{14}$ | 285 | nr | 100 | 59 | 59 | 269 |
| **8** | $CuNC/SiO_2$-$MnO_2$ | 70 | 30 | 77 | 75 | 58 | 270 |
| **9** | HZSM-5/MoVO | 250 | 2 | 100 | 47 | 47 | 266 |
| **10** | V6-SiW/HZSM-5 | 90 | 4 | 100 | 36 | 36 | 271 |
| **11** | H,Fe-MCM-22 | 320 | 10 | 93 | 57 | 53 | 272 |

**Table 6. Different Zeolite-Based Catalysts for the Formation Acrylic Acid from Lactic Acid**

| Entry | Catalyst | Temperature (°C) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|
| **1** | NaY | 350 | 100 | 35 | 35 | 282 |
| **2** | La-NaY | 350 | 100 | 56 | 56 | 282 |
| **3** | $Na_2HPO_4/NaY$ | 350 | 78 | 72 | 56 | 285 |
| **4** | 2.8K/NaY | 325 | 99 | 50 | 50 | 281 |
| **5** | KI/NaY | 325 | 98 | 68 | 67 | 280 |
| **6** | KOH-Ca-NaY | 350 | 100 | 84 | 84 | 286 |
| **7** | $K_{0.94}Na_{0.06}\beta$ | 360 | 94 | 65 | 61 | 287 |
| **8** | K/ZSM-5 | 365 | 99 | 77 | 76 | 288 |
| **9** | 0.5P/ZSM-505AT | 350 | 97 | 78 | 76 | 289 |
| **10** | $NaH_2PO_4$/ZSM-5 | 375 | 100 | 84 | 84 | 290, 291 |
| **11** | K/ZSM-5/NaY | 375 | 100 | 71 | 71 | 292 |
| **12** | $KH_2PO_4$/NaZSM-5 | 330 | 98 | 86 | 84 | 293 |

a much higher acrylic acid selectivity than any previously reported zeolite-based catalysts for oxidative dehydration.[272,273] Iron was selected as the metal for this catalyst due to its $Fe^{2+}/Fe^{3+}$ redox couple as well as due to iron being a more readily available, cheaper and less toxic metal than vanadium, tungsten or molybdenum, hence improving the sustainability aspect of this catalyst.

A different method as to attempt to improve acrylic acid yields involves using two separate catalytic systems for the two steps of the transformation, rather than using a bifunctional catalyst. In this case, the glycerol to acrolein and acrolein to acrylic acid reactions take place in different reactors with various catalysts under different optimized conditions.[259] Several catalysts for the first step have been reported to give good glycerol conversions and acrolein selectivity including cesium doped silicotungstic acid/$Al_2O_3$ (90% acrolein selectivity, 100% conversion), HY zeolite (>99% acrolein selectivity, 89% conversion) and $FePO_4$ (92% acrolein selectivity, 100% conversion).[259,274−276] The second step of the reaction is the oxidation of acrolein, which is typically performed by molybdenum vanadium oxide catalysts. A good example is a vanadium molybdenum mixed oxide supported on silicon carbide synthesized by Liu and co-workers, with acrylic acid yields of up to 96% being obtained.[277] An alternative approach is to use two separate catalysts on a double bed system where there are two separate fixed layers of the catalyst in one reactor. However, the optimum acrylic acid yields for this approach have only been reported to reach 75%.[259,278]

It is noteworthy that acrylic acid yields are higher for these two-step approaches compared to when a multifunctional catalyst is used.[269,270,274−276] However, these approaches have disadvantages such as the need to operate two different reactors and to have to use two valuable catalysts rather than one. Furthermore, the catalytic performance and acrylic acid yields are heavily impacted by the purity of the glycerol.[173,259] This is one of the major challenges in using crude glycerol from the production of biodiesel, as the necessary purifications are an expensive and time-consuming process. These processes are less appealing to commercialize if the large amounts of glycerol produced as a by-product cannot be used.

*3.1.1.2. From Lactic Acid.* Lactic acid is the most common naturally occurring carboxylic acid and is produced *via* the fermentation of sugars, such as glucose and sucrose.[173] In 2020, the global production was reported to be around 370 000 tons per year, with this value being predicted to grow substantially over the next decade.[173,259] The dehydration of lactic acid to produce acrylic acid is challenging because there are several competing reactions such as decarbonylation, decarboxylation, and hydrogenation.[173,254,256,257] If lactic acid is reacted with a Lewis acid or base, acrylic acid will be formed as the major product. However, if lactic acid is reacted in the presence of a Bronsted acid or base, acetaldehyde will be formed as a major side product, while it is also possible in basic conditions for 2,3-pentadione to be formed.[279] Biochemical approaches have been explored in which acrylic acid has been formed in a reaction catalyzed by CoA transferase and lactyl-CoA-dehyratase, which were obtained from *Clostridium propionicum*.[254,256,257] However, this anaerobic process gives a low yield of acrylic acid. Many catalysts have been studied for the production of acrylic acid from lactic acid, with zeolites having been the most widely used due to their high surface area.[173] NaY, $\beta$ and ZSM-5 zeolites have been the most vastly studied classes of zeolite-based catalysts for the transformation of lactic acid into acrylic acid (Table 6).[173] Of these, NaY

Table 7. Different Phosphate-Based Catalysts for the Formation Acrylic Acid from Lactic Acid

| Entry | Catalyst | Temperature (°C) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|
| **1** | HAP-3 | 375 | 100 | 60 | 60 | 295 |
| **2** | HAP$_{1.62}$-360 | 360 | 84 | 74 | 62 | 296 |
| **3** | Ca-HAP$_{(1.55)}$NaOH | 350 | 90 | 87 | 78 | 297 |
| **4** | CP-3 | 375 | 100 | 78 | 78 | 298 |
| **5** | $K_2HPO_4$/CaOP | nr | 91 | 93 | 85 | 173 |
| **6** | $K_2HPO_4$/BaOP | 350 | 91 | 93 | 85 | 299, 300 |
| **7** | $K_2HPO_4$/SrOP | 380 | 100 | 72 | 72 | 301 |
| **8** | BaPP | 400 | 100 | 76 | 76 | 302 |
| **9** | $CaSO_4$ | 400 | >99 | 69 | 69 | 303 |
| **10** | $BaSO_4$ | 400 | >99 | 66 | 66 | 303 |

zeolites have been the most explored catalysts for the dehydration of lactic acid, especially when modified with potassium, barium or rare earth metals (including lanthanum, cerium, europium and samarium).[256,280−284]

The effect of the Si/Al ratio in NaY zeolites has also been investigated, with higher Si to Al favoring the formation of acetaldehyde, thus decreasing the selectivity toward acrylic acid.[279] Attempts to modify NaY catalysts include doping with rare earth metals (Table 6, entries 1 and 2).[282] Doping with 2 wt % lanthanum, cerium and europium increased the acrylic acid selectivity from 35% to 56%, 46% and 40%, respectively.[282] Modifying NaY zeolites with alkali phosphates also had a positive impact on the reaction by decreasing surface acidity, thus reducing side reactions. The acrylic acid selectivity further increased up to 72% for the 14 wt % $Na_2HPO_4$/NaY catalyst at 350 °C (Table 6, entry 3).[285] Doping with potassium led to an increase in both conversion and acrylic acid selectivity from 96% and 15% to 99% and 50%, respectively for the catalyst 2.8K/NaY after a 360 min reaction time at 325 °C (Table 6, entry 4).[281] In a different study, the NaY zeolites were doped with potassium salts which led to an even greater increase in acrylic acid selectivity.[280] The optimum value for acrylic acid selectivity that was achieved to be 68% when a KI/NaY catalyst was used while the lactic acid conversion was 98% (Table 6, entry 5). As for the alkali phosphates, potassium doping decreased the acidity of the catalysts, hence reducing unwanted side reactions.

Zhang *et al.* achieved even higher acrylic acid selectivity by doping NaY zeolites with alkali and alkaline earth metals.[286] An optimum acrylic acid selectivity of 84% was obtained for the KOH-Ca-NaY catalyst (Table 6, entry 6). This was a significantly larger value than those of the NaY, KOH-NaY or Ca-NaY catalysts, which had selectivity values of 43%, 63% and 70%, respectively. The stability of the catalyst was further demonstrated, as after 4 long reaction cycles, an acrylic acid selectivity of 82% was obtained. While modified NaY zeolites show promising increases in the reaction selectivity, the problem of catalyst deactivation remains a challenge. Näfe *et al.* reported that the buildup of acidic hydrocarbons, such as lactic acid and acrylic acid commonly leads to catalyst deactivation. It was reported that substituting the $Na^+$ ions for $K^+$ or $Cs^+$ can reduce such deactivation due to steric hindrance.[294]

Other types of zeolites have been explored for catalysis in the formation of acrylic acid including β-zeolites and ZSM zeolites.[173] Alkali metal doped β-zeolites reached acrylic acid selectivity and conversion values of up to 65% and 94%, respectively (Table 6, entry 7).[287] A general trend was observed where potassium and cesium doped zeolites had higher acrylic acid selectivity when compared to lithium and sodium doped zeolites. Yuan *et al.* studied alkali metal doped ZSM-5 zeolites, whereby the potassium doped catalyst gave an optimum acrylic acid selectivity of 77% at 99% conversion (Table 6, entry 8).[288] All of the alkali metal doped catalysts gave significantly higher acrylic acid selectivity values than the HZSM-5 catalyst which, while having a high lactic acid conversion of 99.9%, had a selectivity of only 1.4%. Furthermore, ZSM-5 doped with NaOH and $Na_2HPO_4$ achieved similar results with an optimized conversion and acrylic acid selectivity of 97% and 78%, respectively for a 9 h reaction at 350 °C (Table 6, entry 9).[289] When the ZSM-5 catalyst was treated with NaOH and doped with 7% $NaH_2PO_4$ an improved selectivity of 84% at full conversion was obtained (Table 6, entry 10).[290] The improvement in performance was attributed to the phosphate doping changing the number of acid sites and increasing the basicity. The use of mixed zeolite catalysts has also been investigated. A K/ZSM-5/NaY catalyst achieved a 71% acrylic acid selectivity at full conversion in a reaction run at 375 °C (Table 6, entry 11).[292] A final example of a zeolite catalyst investigated a NaZSM-5 catalyst, which managed to achieve a high acrylic acid selectivity of 86% with a 98% lactic acid conversion when doped with 4 mmol $KH_2PO_4$ (Table 6, entry 12).[293]

Phosphate catalysts (e.g., calcium hydroxyapatite, HAP) have also been used in the production of acrylic acid from lactic acid.[259] The most important property in determining catalytic performance is the balance of acidic and basic sites. Strongly acidic sites favored unwanted side reactions and so moderate or weakly acidic sites were important for optimal catalytic performance.[259] HAP catalysts have both weakly acidic and weakly basic sites which favored dehydration and the acid/base properties can be tuned by altering the Ca/P ratio.[259,295] For the catalyst HAP-3, which has a Ca/P ratio of 1.3, an optimized acrylic acid selectivity of 60% was obtained for a reaction at 375 °C (Table 7, entry 1).[295] Yan *et al.* found that increasing the Ca/P ratio led to an increase in the acrylic acid selectivity, with a catalyst with a Ca/P ratio of 1.62 achieving an optimum acrylic acid selectivity of 74% (Table 7, entry 2).[296] However, a lower lactic acid conversion of 84% was observed. The correlation between the Ca/P ratio and acrylic acid selectivity was attributed to the ratio of acid/base sites. Matsuura *et al.* optimized conditions for the use of a Ca-HAP(1.55)$_{NaOH}$ catalyst and achieved an optimum acrylic acid yield of 78% and a lactic acid conversion of 90% (Table 7, entry 3).[297] This catalyst had a Ca/P ratio of 1.55 and was doped with 1.4 wt % of sodium. The $Na^+$ ions played an important role in replacing deficient $Ca^{2+}$ ions and this led to increased catalytic performance.

As well as HAPs, alkaline earth metal pyrophosphates (MPP) and orthophosphates (MOP) have been reported as catalysts in the production of acrylic acid from lactic acid.[173] Ghantani and co-workers showed an optimum acrylic acid selectivity of 78% for a reaction at 375 °C with the catalyst CP-3 (an MPP), which had a low Ca/P ratio of 0.76 (Table 7, entry 4).[298] The increased selectivity was attributed to the acid/base balance at low Ca/P ratios which resulted in the increased formation of a calcium lactate intermediate. MPPs and MOPs can be doped to improve their catalytic activity. For example, calcium orthophosphate has been doped with $K_2HPO_4$ which resulted in a very high acrylic acid selectivity of 93% along with a lactic acid conversion of 91% (Table 7, entry 5).[173] Metals other than calcium can be used in MPPs and MOPs to obtain acrylic acid in comparable yields. In one example, a $K_2HPO_4$ doped BaOP catalyst was used in a one-pot conversion of lactic acid to acrylic acid, with a conversion and selectivity of 91% and 93%, respectively (Table 7, entry 6).[299,300] Tang and co-workers obtained an optimal acrylic acid selectivity of 72% when a SrPP catalyst doped with 0.1 wt % $H_3PO_4$ was used at 380 °C (Table 7, entry 7).[210,301] It was also shown that BaPP achieved an acrylic acid selectivity of 76% at 400 °C (Table 7, entry 8).[302]

Other phosphate catalysts that have been explored include lanthanum and cerium phosphates. However, acrylic acid selectivity values were relatively low at 50% and 64%, respectively.[173,304,305] As well as phosphates, sulfate salts and doped sulfate salts have been explored as catalysts. Peng and co-workers investigated the use of metal sulfates as catalysts for the production of acrylic acid from lactic acid.[303] Magnesium, barium and calcium sulfates had higher catalytic performances than aluminum, nickel or zinc sulfates. This was attributed to the calcium, magnesium and barium salts being weaker acids, while the other sulfates tested were more acidic and so favored unwanted side reactions. Calcium sulfate achieved slightly better results than barium sulfate (i.e., 69% vs 66% selectivity) but the barium salt was found to be the most stable catalyst (Table 7, entries 9 and 10).

*3.1.1.3. From 3-Hydroxypropanoic Acid.* A structural isomer of lactic acid, 3-hydroxypropionic acid (3-HPA), is also produced through glucose fermentation or from glycerol.[257] Furthermore, acrylic acid can be prepared *via* the dehydration of 3-HPA. Different classes of catalysts have been used in the dehydration of 3-HPA to acrylic acid, including Bronsted acids, metal oxides or zeolite catalysts.[173] The thermal dehydration of 3-HPA produced an 80% yield of acrylic acid, using reduced pressure, a sulfuric acid (or phosphoric acid) catalyst and copper powder as an inhibitor, at elevated temperatures between 140 and 160 °C.[306] If an alcohol is added into this reaction, the alkyl acrylate can be formed directly.[307] Heterogeneous catalysts have been reported to increase the yield of production, for example, a yield of 96% was achieved when a $NaH_2PO_4$ on silica catalyst was used.[308] Gas phase dehydration reactions have also been reported using metal oxide or zeolite catalysts, with conversions of 97% being achieved when $Al_2O_3$ was used as the catalyst.[309] An example of a metal oxide catalyst was the use of Cu-Ba-CrO as a catalyst.[259,310] Full acrylic acid selectivity was reported when used in a batch reactor, but a lower 3-HPA conversion of 63% was observed. Alumina and silica catalysts resulted in a 97% acrylic acid yield in a reaction at 250 °C.[311] Other studies showed that $TiO_2$ could also be an effective catalyst for this reaction, with a selectivity for acrylic acid of 99%.[312,313] Different solid acid catalysts such as, HY, ZSM-5, $\beta$, MCM-41 and silica gel were explored by Li *et al.*[314] The silica gel proved to be the best catalyst for this reaction, with an optimal acrylic acid yield of >99%. There was also very limited deactivation over 200 h, with excellent catalytic stability being shown.

The performance of the reaction is heavily influenced by the purity of the 3-HPA starting material.[315] When pure synthesized 3-HPA was reacted over a bentonite catalyst, a high acrylic acid yield (i.e., 89%) was observed. However, when a less pure bio-3-HPA was used under the same conditions, a much lower acrylic acid yield of 68% was reached. When bio-3-HPA was purified with a cation exchange resin before the reaction, 3-HPA conversion and acrylic acid selectivity were 95% and 98%, respectively. While high catalytic performance was achieved, it should be noted that the purification has significant disadvantages including added cost and increased time consumption.[316] While there have been promising results in terms of acrylic acid yields from 3-HPA, another problem is that the formation of the starting material *via* fermentation is challenging and has deemed the route unviable to industrially produce acrylic acid from 3-HPA.[259]

*3.1.1.4. From Allyl Alcohol.* Acrylic acid can also be formed from allyl alcohol, which is an intermediate in the production of acrylic acid from glycerol.[173] Molybdenum vanadium mixed oxides can catalyze this reaction, with the heptagonal channels present in the catalyst structure providing active sites for the oxidation of both allyl alcohol and acrolein to acrylic acid.[317] The maximum acrylic acid yield was 73% when an orthorhombic $MoVO_x$ catalyst was used at 350 °C. However, the main problem with using molybdenum vanadium mixed oxide catalysts is that they are unstable and deactivate over time. As for the oxidative dehydration of glycerol to form acrylic acid, the addition of a third metal, such as tungsten, copper and iron, has been shown to improve the catalytic activity and stability.[173,263] The effects of doping $MoVO_x$ with copper, iron and tungsten on the catalytic performance were investigated.[318] The best catalyst for the oxidation of allyl alcohol was shown to be the iron doped catalyst, MoVFeO, which achieved an acrylic acid yield of 83% at 350 °C. The high activity of this catalyst was attributed to the prevention of the isomerization of the allyl alcohol, which would result in undesired side reactions.

An alternative to the mixed metal oxide catalysts is liquid oxidation using noble metal nanoparticles supported on metal oxides.[319] Gold nanoparticles supported on $CeO_2$ showed the best acrylic acid selectivity of 51% at full conversion. $TiO_2$, ZnO, $Fe_2O_3$ and carbon-based supports all achieved significantly lower acrylic acid yields, thus highlighting the importance of the support on the catalytic activity. One advantage of this procedure was the significantly lower operating temperature of 50 °C, compared to the temperatures >300 °C that were required for the metal mixed oxide and zeolite catalysts. Kim and co-workers improved on the acrylic acid selectivity of the Au/$CeO_2$ catalyst by investigating the different morphologies of catalysts.[320] The octahedral $CeO_2$ support provided a higher catalytic activity compared to the cubic or rod-shaped geometries, with the optimum acrylic acid selectivity being 92% at full conversion. The octahedral geometry has the highest surface area, which led to a greater catalytic performance. Once again, this procedure had the advantage of a low operating temperature of 25 °C. One of the

**Table 8. Different Keggin-Based Catalysts for the Transformation of Isobutane to Methacrylic Acid**

| Entry | Catalyst | Temperature (°C) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|
| **1** | $H_3PMo_{12}O_{40}$ | 340 | 7 | 4 | 0.28 | 328 |
| **2** | $H_3PMo_{12}O_{40}$-Py | 300 | 12 | 58 | 7 | 329 |
| **3** | $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ | 340 | 16 | 24 | 4 | 330 |
| **4** | $Cs_2HPMo_{12}O_{40}$ | 340 | 11 | 34 | 4 | 330 |
| **5** | $Cs_{2.5}Ni_{0.08}H_{0.34}PMo_{12}O_{40}$ | 340 | 24 | 27 | 7 | 330 |
| **6** | $(NH_4)_3PMo_{12}O_{40}$ | 352 | 5 | 42 | 2 | 331 |
| **7** | $H_4PVMo_{11}O_{40}$ | 350 | 11 | 30 | 3 | 332 |
| **8** | $Cs_{0.75}H_{0.25}VO[PMo_{12}O_{40}]$ | 350 | nr | 76 | nr | 333 |
| **9** | $Cs_2V_{0.3}PMo_{11}O_{40}$ | 330 | 6 | 55 | 3 | 334 |
| **10** | $Cs_{1.7}(NH_4)_{1.3}HPMo_{11}VO_{40}$ | 340 | 10 | 43 | 4 | 335 |
| **11** | $(NH_4)_3HPMo_{11}VO_{40}/Cs_3PMo_{12}O_{40}$ | 340 | 14 | 47 | 6 | 336 |
| **12** | $Cs_2V_{1.3}Cu_{0.2}PMo_{12}O_{40}$ | 350 | 13 | 48 | 6 | 337 |
| **13** | $Cs_2HPMo_6O_{12}$ | 350 | 9 | 44 | 4 | 337 |

issues with the Au/$CeO_2$ catalyst, however, is that it requires 3M NaOH. Different catalysts that operate in base free conditions have been investigated, which has two main advantages. First, the amount of waste is reduced and second corrosion in the reactor is limited.[321] However, the catalytic performance was significantly lower with the highest acrylic acid yield being 43% when 4 wt % Pd NP/C(sol) catalyst was used in a 6 h reaction at 100 °C.

*3.1.1.5. From Acetic Acid.* Acetic acid can be used to synthesize acrylic acid through an aldol reaction with formaldehyde. Both of these reactants can be produced sustainably through the fermentation of biomass.[322,323] The main class of catalysts for this reaction are vanadium phosphorous oxides. Hu and co-workers achieved an optimum acrylic acid selectivity of 93% for a vanadium phosphate catalyst on a SBA-15 support, which had a P/V ratio of 2.4, at 330 °C.[324] However, the conversions of acetic acid were very low. By increasing the reaction temperature to 370 °C the conversion increased to 57% but the acrylic acid selectivity fell to 78%. The catalytic performance of different catalysts was attributed to the affect the different P/V ratios had on the acid/base characteristics of the catalysts. By doping a vanadium phosphate catalyst with cerium, Wang and co-workers achieved an acrylic acid yield of 74% at 380 °C.[325] The addition of metal cations increased the $V^{5+}/V^{4+}$ ratio which promoted a higher catalytic performance. Liu and co-workers investigated a VPO catalyst supported on a siliceous mesostructured cellular foam (MCF).[326] The $V^{5+}/V^{4+}$ ratio of the catalyst was tunable by the VPO loading, while during the catalyst synthesis, ammonia was used to induce a partial reduction of $V^{5+}$. Using this catalyst, the combined yield of acrylic acid and methyl acrylate was 84% at a reaction temperature of 360 °C.

### 3.1.2. Methacrylic Acid.

*3.1.2.1. From Isobutane.* Isobutane can be produced from biomass through a thermo-catalytic process as well as through the fermentation of sugars.[327] To produce MAA from isobutane, first the oxidation of isobutane to the intermediate methacrolein occurs, before further oxidation resulting in the formation of methacrylic acid.[173] The most frequently used class of catalysts used for the oxidation of isobutane are Keggin-type catalysts, which are based on a $H_4Pmo_{12}O_{40}$ structure. The structure consists of a phosphorus atom at the center of a tetrahedron that is neighbored by $MoO_6$ units. The acidity/basicity of the catalyst can be tuned through the addition of different metals.[173] For example, Mizuno and co-workers showed that an unmodified $H_3Pmo_{12}O_{40}$ catalyst showed very low activity and selectivity, with a conversion and MAA selectivity of just 7% and 4%, respectively, being obtained (Table 8, entry 1).[328] The catalyst selectivity was significantly improved by using a pyridinium 12-molybdophosphate ($H_3Pmo_{12}O_{40}$-Py).[329] An optimum MAA selectivity of 58% was obtained at 12% isobutane conversion at 300 °C (Table 8, entry 2). An increased temperature of 340 °C showed an increased conversion of 47% but with a significant drop in selectivity to 18%. The better performance of this catalyst was attributed to the reduced molybdophosphate and oxygen deficient anions providing suitable activating sites for both oxygen and isobutane.

The selectivity and activity of the catalysts can also be improved through doping with other metals, for example, cesium, vanadium, and copper.[330] Keggin-type catalysts can be doped with cesium to improve catalytic activity. The catalyst $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ showed a MAA selectivity of 24% (at 16% conversion), while the catalyst with slightly less cesium, $Cs_2HPMo_{12}O_{40}$, had an increased MAA selectivity of 34% but at lower conversion (i.e., 11%, Table 8, entries 3-4). Further modification by addition of a nickel dopant showed an increase in activity without too much change to the MAA selectivity, with a selectivity of 27% being obtained at 24% conversion (Table 8, entry 5).[330] It was shown that doping the catalyst with nickel improved the catalyst performance more significantly than when $Mn^{2+}$, $Fe^{3+}$, $Cu^{2+}$ or $Co^{2+}$ were used.[338] Replacing the protons with ammonium cations significantly increased the selectivity (42%) compared to the unmodified catalyst, while not improving the activity (5% conversion) under isobutane rich conditions (Table 8, entry 6).[331] However, under isobutane deficient conditions, the selectivity fell back to a value comparable with the unmodified catalyst (4%). The difference in selectivity for the two different conditions was attributed to the redox reaction between ammonia and $Mo^{6+}$ occurring at high isobutane concentrations, which positively impacted the catalytic performance.

Partially substituting molybdenum with vanadium led to an increase in selectivity of the catalyst.[332] The vanadium occupies a cationic site and becomes an active site for the oxidation of isobutane. For the catalyst $H_4PVMo_{11}O_{40}$, a conversion and MAA selectivity of 11% and 30% were obtained respectively at 350 °C (Table 8, entry 7). Further doping with cesium led to an improved selectivity of 76% (Table 8, entry 8).[333] He and co-workers investigated various catalysts containing both cesium and vanadium, and obtained an optimum selectivity of 55% with a conversion of 6% at 330 °C using a $Cs_{2.0}V_{0.3}PMo_{11}VO_{40}$ catalyst (Table 8, entry 9).[334]

### Table 9. Different Homogeneous Catalysts That Were Used for the Transformation of Various Biobased Carboxylic Acids to Methacrylic Acid

| Entry | Catalyst | Substrate | Temperature (°C) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| **1** | No catalyst | Itaconic acid | 400 | 92 | 33 | 30 | 341 |
| **2** | No catalyst | Citric acid | 320 | 100 | 7 | 7 | 341 |
| **3** | 10 mM NaOH | Itaconic acid | 360 | 100 | 72 | 72 | 341 |
| **4** | 0.5 M NaOH | Mesaconic acid | 320 | 100 | 52 | 52 | 343 |
| **5** | 0.5 M NaOH | Citraconic acid | 320 | 98 | 40 | 39 | 343 |
| **6** | Ru carbonyl proprionate | Itaconic acid | 225 | 34 | 100 | 34 | 344 |

### Table 10. Different Heterogeneous Catalysts That Were Used for the Transformation of Various Biobased Carboxylic Acids to Methacrylic Acid

| Entry | Catalyst | Substrate | Temperature (°C) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| **1** | Pd/C/0.1 M NaOH | Itaconic acid | 250 | 89 | 47 | 42 | 345 |
| **2** | $Pt/Al_2O_3$ | Itaconic acid | 250 | 80 | 84 | 67 | 345 |
| **3** | $Pd/Al_2O_3$ | Citric acid | 250 | 100 | 41 | 41 | 345 |
| **4** | $Pt/Al_2O_3$ | Aconitic acid | 250 | 100 | 48 | 48 | 345 |
| **5** | $BaAl_{12}O_{19}$ | Itaconic acid | 250 | 100 | 50 | 50 | 346 |
| **6** | $BaAl_{12}O_{19}$ | Citric acid | 250 | 100 | 50 | 50 | 346 |
| **7** | $BaAl_{12}O_{19}$ | Aconitic acid | 250 | 85 | 51 | 43 | 346 |
| **8** | Hydrotalcite | 2-HIBA | 275 | 80 | 89 | 72 | 347 |
| **9** | LaHA | Itaconic acid | 250 | 100 | 12 | 12 | 348 |
| **10** | CaHA | Itaconic acid | 250 | 100 | 38 | 38 | 348 |
| **11** | MgHA | Itaconic acid | 250 | 100 | 40 | 40 | 348 |
| **12** | BaHA | Itaconic acid | 250 | 100 | 50 | 50 | 348 |

The key finding of this study was that the precursors and methods used to synthesize the catalysts were important for good catalytic performance. The optimal catalyst was obtained from vanadyl sulfate and showed good $V^{4+}/V^{5+}$ and $Mo^{5+}/Mo^{6+}$ surface ratios, along with high acidity leading to good performance.

Catalysts containing both cesium and ammonium ions have also been studied. The best results were achieved with the catalyst $Cs_{1.7}(NH_4)_{1.3}HPMo_{11}VO_{40}$ at 340 °C, with a MAA selectivity of 43% reached at 10% conversion (Table 8, entry 10).[335] The key factor in catalytic performance was thought to be the balance between acidity and specific surface area. The catalytic loading for a $(NH_4)_3HPMo_{11}VO_{40}$ catalyst was investigated and shown to have a significant impact on catalytic activity.[336] While at 10 wt %, the reaction did not occur, increasing the catalyst loading increased the selectivity of the oxidation. At 50 wt %, the optimum results of a MAA selectivity of 47% at 14% isobutane conversion was obtained (Table 8, entry 11). Catalysts doped with $Cu^{2+}$ and $VO^{2+}$ have also been developed and achieved an optimal MAA selectivity of 48% at 13% isobutane conversion using a $Cs_2V_{0.3}Cu_{0.2}PMo_{12}O_{40}$ catalyst at 350 °C (Table 8, entry 12).[337] This was a slight improvement on the undoped $Cs_2HPMo_6O_{12}$ catalyst, for which a MAA selectivity of 44% at 9% isobutane conversion was observed (Table 8, entry 13). The improvement in catalytic activity was attributed to the $Cu^{2+}$ and $VO^{2+}$ ions in the secondary structure assisting the re-oxidation of $Mo^{5+}$ to $Mo^{6+}$. Doping with other metals was attempted, including iron, nickel and cerium, but none resulted in superior results to the copper doped catalyst.

A small number of mixed oxide catalysts have also been used in the oxidation of isobutane to methacrylic acid.[339,340] The catalyst with the highest performance was a $MoV_{0.3}Te_{0.23}Ce_{0.2}$ catalyst, which achieved a combined methacrylic acid and methacrolein selectivity of 20% when an isobutane conversion of 20% was reached.[339] This showed a significant improvement on the catalyst without the cerium (12% selectivity at 15% conversion), which was attributed to cerium's high oxygen storage potential hence improving oxygen mobility throughout the catalyst. It was also noted that cerium can participate in a redox reaction with molybdenum and help in the reoxidation of the catalyst.

While there have been many studies into different catalysts to produce methacrylic acid from isobutane, it is plagued by extremely low yields. While doping catalysts led to increases in selectivity, all examples show extremely low isobutane conversions (i.e., <24%). It is also noteworthy that moderately high temperatures are required to achieve these poor yields, thereby impeding the sustainability of this process. Until these techniques have been developed further to boost methacrylic acid yields, the production of methacrylic acid from isobutane remains rather unfeasible on an industrial scale.

*3.1.2.2. From Carboxylic Acids.* Besides isobutane, bio-based MAA can also be produced from bio-based carboxylic acids, such as itaconic acid or citric acid (which can be produced through the fermentation of carbohydrates), through a dehydration and decarboxylation reaction.[173] Both homogeneous and heterogeneous catalysts have been investigated for use in the production of MAA from carboxylic acids (Table 9 and Table 10).

In general, homogenous catalysts results in increased yields when compared to heterogenous catalysts but have the disadvantage of being more difficult to be separated from reaction products. A specific example of using homogeneous catalysts to produce MAA has been reported by Carlsson and co-workers using citric acid and itaconic acid as substrates.[341] For itaconic acid, when no catalyst was used at 400 °C, a yield of 30% was obtained for MAA at 92% conversion (Table 9, entry 1). The reaction was carried out under supercritical water conditions and they reported that the decarboxylation of acids was assisted by the dissociation of water into hydronium and hydroxide ions. For the reaction of citric acid with no catalyst present at 320 °C, the reaction went to full conversion but the yield of MAA was only 7% (Table 9, entry 2). It was also found that the reaction strongly depended on the pH with both neutral and acidic conditions promoting unwanted side products, such as acetic acid and acetone, at high temperatures.[341,342] Conditions that were too basic were also detrimental to the reaction by quenching the decarboxylation process.[341,342] However, the addition of a small amount of base was found to improve results for the reaction with itaconic acid. When 10 mM NaOH was added, full conversion was obtained at 360 °C, with a 72% yield of MAA (Table 9, entry 3). In contrast, the addition of 10 mM NaOH to the citric acid reaction showed no improvement on the selectivity of MAA production.

Other bio-based carboxylic acids have been studied to produce MAA, and these include mesaconic acid and citraconic acid.[343] When reacted in 0.5 M NaOH at 320 °C, the yields of MAA were 52% and 40% for mesaconic and citraconic acid, respectively (Table 9, entries 4 and 5). More recently, a ruthenium carbonyl propionate catalyst was used to further improve the selectivity for MAA in the reaction of itaconic acid.[344] This system greatly improved the selectivity for MAA, with 100% selectivity being observed for a 1.5 h reaction at 225 °C, containing 0.1 wt % of catalyst and 0.5 mol % of $PPh_3$. This resulted in an overall yield of MAA of 34% (Table 9, entry 6).

In contrast to homogenous catalysts, using heterogeneous catalysts enables the use of more expensive catalysts as they can often be recovered and recycled. Hence, the use of various platinum and palladium catalysts for the transformations of carboxylic acids to MAA has been investigated.[345] When itaconic acid was used with a Pd/C catalyst and 0.1 M NaOH at 250 °C, a MAA selectivity of 47% was obtained at 89% conversion (Table 10, entry 1). By using a $Pt/Al_2O_3$ catalyst for the reaction of itaconic acid, the selectivity was significantly improved to 84% (at 80% conversion, Table 10, entry 8). $Al_2O_3$ supported Pd and Pt catalysts were also used to convert citric acid and aconitic acid, respectively. However, these resulted in lower methacrylic acid yields of 41% and 48% compared to the reaction of itaconic acid with $Pt/Al_2O_3$ (Table 10, entries 3 and 4). $BaAl_{12}O_{19}$ catalyst was also investigated as a catalyst for the conversion of itaconic acid, citric acid and aconitic acid into MAA (Table 10, entries 5–7).[346] Itaconic acid and citric acid both reached full conversion with a 50% selectivity for MAA, while the reaction of aconitic acid obtained a 51% MAA selectivity at 85% conversion. Hydrotalcite was used as a catalyst in the production of MAA from itaconic acid, citric acid and 2-hydroxyisobutyric acid (2-HIBA).[347,348] While a MAA yield of 72% was achieved at 80% conversion for the reaction of 2-HIBA (Table 10, entry 8), lower yields of 23% and 21% were recorded for itaconic and citric acid, respectively. Finally, various hexaluminate catalysts have been used for the conversion of itaconic acid into methacrylic acid (Table 10, entries 9-12).[348] Barium hexaluminate showed the highest catalytic activity, achieving a 50% MAA selectivity at full conversion.

### 3.1.3. Alkyl (Meth)acrylates.

*3.1.3.1. From Acrylic Acid.* Industrially, alkyl acrylates, such as methyl acrylate, are produced *via* an esterification reaction with acrylic acid and an excess of alcohol in the presence of a strong acid (e.g. sulfuric acid).[259] To obtain high yields, an excess of alcohol is typically required, but this leads to problems with purification of the end product. Another challenge for the esterification of acrylic acid is the production of unwanted side products, such as dimers and trimers of acrylic acid formed *via* Michael addition and alkyl alkoxy esters.[259]

Alternative methods have been sought which reduce the need to use an alcohol in a large excess. One such method uses dimethyl carbonate instead of an alcohol. A high yield of 91% methyl acrylate was achieved when aluminum triflate was used as a catalyst.[259,349,350] A different $ZrOCl_2{\cdot}8H_2O$ catalyst was used for the esterification of acrylic acid and methanol, producing methyl acrylate in a 71% yield.[351] This catalyst offered the significant advantage over strong acid catalysts (e.g. sulfuric acid) in that it allowed acrylic acid and methanol to be used in an equimolar ratio, thus overcoming problems with purification of the product.[351] While improved methods for the esterification of acrylic acid have been made, possible alternative routes from feedstock directly, without the need for an esterification of acrylic acid, have been highly sought after, with some of these being displayed in Figure 12. Examples of feedstock for the synthesis of alkyl acrylates include 3-HPA, glycerol, acetic acid and lactic acid.

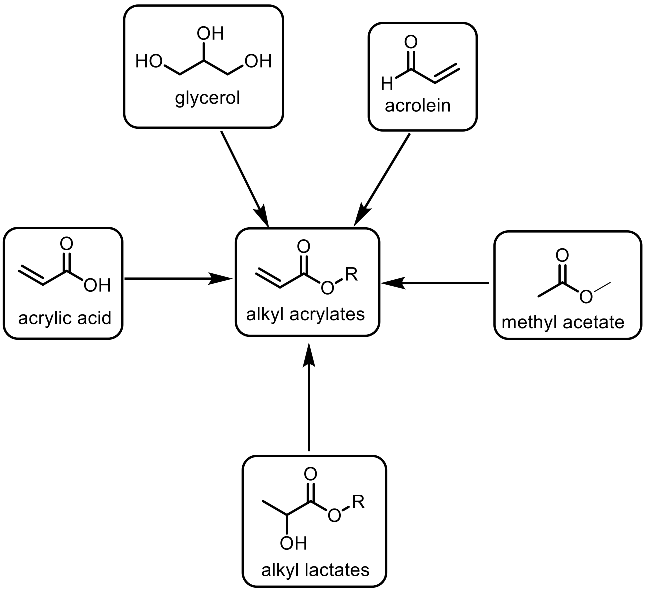


**Figure 12.** Various routes to produce alkyl acrylates from bio-derived feedstocks.

*3.1.3.2. From Alkyl Lactates.* The hydroxyl and carboxylic acid functional groups in lactic acid make it a useful precursor in the production of different chemicals such as acrylic acid, lactate esters and 1,2-propanediol.[256] While the use of lactic acid in the synthesis of bio-acrylic acid has already been discussed (section 3.1.1.2), lactate esters can also be used in the synthesis of acrylate and methacrylate monomers. Lactate esters can be used to produce alkyl acrylates through two methods. First, the lactate esters can undergo a dehydration reaction, similar to the transformation of lactic acid into acrylic acid. Second, the hydroxyl group of the lactate ester can react with a coupling agent such as acryloyl chloride to form more complex acrylates.

Although lactic acid can be made through chemical synthesis, it is commercially produced from the fermentation of glucose.[257] Whereas conventional production uses a large

**Table 11. Different Catalysts Used to Convert Alkyl Lactates to Alkyl Acrylates**

| Entry | Catalyst | Substrate | Temperature (°C) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| **1** | HAP | Ethyl lactate | nr | 55 | 18 | 10 | 354, 355 |
| **2** | HAP/Na-CaPP (50:50) | Methyl lactate | 390 | 91 | 5 | 5 | 356 |
| **3** | HAP/Na-CaPP (50:50) | Ethyl lactate | 390 | 82 | 5 | 4 | 356 |
| **4** | HAP/Na-CaPP (50:50) | Butyl lactate | 390 | 76 | 5 | 4 | 356 |
| **5** | CaOP/CaPP (50:50) | Methyl lactate | 390 | 91 | 5 | 5 | 357 |
| **6** | CaOP/CaPP (50:50) | Ethyl lactate | 390 | 57 | 5 | 3 | 357 |
| **7** | CaOP/$CaSO_4$ | Methyl lactate | 400 | 50 | 53 | 27 | 358, 359 |
| **8** | $CaSO_4$/$CuSO_4$.5$H_2O$/$Na_2HPO_4$/$KH_2PO_4$ | Methyl lactate | 400 | 76 | 26 | 20 | 255 |
| **9** | NaX | Methyl lactate | 240 | 99 | 93 | 92 | 360, 361 |
| **10** | Cs-NaX | Methyl lactate | 300 | 70 | 43 | 30 | 362 |
| **11** | La-Montmorillonite/NaY | Methyl lactate | 320 | 88 | 59 | 52 | 363 |

amount of sulfuric acid and produces large amounts of calcium sulfate, new technologies have been developed in membrane separation and purification methods to try and increase the sustainability of production.[257,352,353] Alkyl lactates are typically synthesized from lactic acid *via* esterification. While the conversion of lactic acid to acrylic acid has been vastly studied, the conversion of alkyl lactates has been less explored. The same classes of catalysts that are used for the synthesis of acrylic acid from lactic acid, can be used to produce alkyl acrylates. For pure HAP catalysts, there is a significant decrease in conversion (99% vs 55%) and selectivity (68% vs 18%) when the feedstock was changed from lactic acid to ethyl lactate (Table 11, entry 1).[354,355] Hong and co-workers observed a decrease in lactate conversion as the alkyl chain increased in length with the lactate conversions of methyl, ethyl and butyl lactates having conversions of 91%, 82% and 76% when using a mixed HAP/Na-CaPP (50/50) catalyst.[356] However, both the alkyl acrylate and acrylic acid selectivity values remained similar at about 5% and 75% respectively (Table 11, entries 2−4). Hong also investigated CaOP-CaPP(50/50) composite catalysts at 390 °C for methyl lactate and ethyl lactate.[357] Once again the methyl lactate proceeded with higher conversion (91%) compared to ethyl lactate (57%), but the difference was more pronounced with this catalyst. The same problems with selectivity were observed for both of the alkyl acrylates (only 5% selectivity) while the values for acrylic acid selectivity remained high at 75% and 79% for the reactions with methyl lactate and ethyl lactate, respectively (Table 11, entries 5 and 6). A CaOP/$CaSO_4$ catalyst was shown to not have the same issues in terms of selectivity.[358,359] For a reaction with methyl lactate at 400 °C, a MA selectivity of 53% was achieved, while no acrylic acid selectivity was reported. However, this reaction did proceed with a significantly lower methyl lactate conversion of 50% (Table 11, entry 7). Zhang *et al.* explored the use of $CaSO_4$ catalysts with different promoters.[255] The catalyst showing the highest performance was a $CaSO_4/CuSO_4{\cdot}5H_2O/Na_2HPO_4/KH_2PO_4$ system with a ratio of 150:13.78:2.5:1.2. In a reaction with methyl lactate, a conversion of 76% was achieved while selectivity values for acrylic acid and methyl acrylate of 54% and 26%, respectively were obtained (Table 11, entry 8).

Zeolites have also been used to catalyze the dehydration of alkyl lactates. The best catalytic performance reported was obtained with a NaX catalyst at 240 °C when a methyl lactate conversion of 99% was achieved along with selectivity values for methyl acrylate and acrylic acid of 93% and 2%, respectively (Table 11, entry 9).[360,361] This shows more promising results in terms of methyl acrylate selectivity than any of the Ca-based catalysts. However, since patented, these promising results have yet to be replicated by others.[259] Other zeolites that result in a higher methyl acrylate selectivity compared to acrylic acid include Cs-NaX and La-montmorillonite/NaY (Table 11, entries 10 and 11).[362,363]

An alternative method to form acrylates from lactate esters involves the reaction of the hydroxyl group with a coupling agent. Bensabeh *et al.* synthesized ethyl lactate acrylate *via* two different approaches, while also synthesizing methyl lactate acrylate and butyl lactate acrylate through the first approach.[364] The starting material, ethyl lactate, can be synthesized from lactic acid through a reaction with ethanol catalyzed by Cal-B in dioxane with 85% yield.[365,366] The two approaches for the synthesis of ethyl lactate acrylate are displayed in Figure 13.

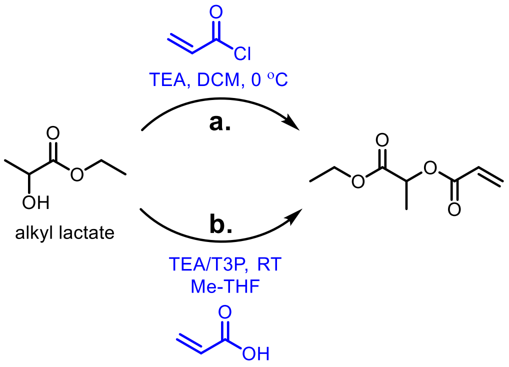


**Figure 13.** Two synthetic routes to synthesize acrylate monomers from alkyl lactates using acryloyl chloride (a) and a more sustainable route using acrylic acid (b).

Methyl lactate acrylate, ethyl lactate acrylate and butyl lactate acrylate were synthesized by reacting the alkyl lactates with acryloyl chloride in the presence of triethylamine at 0 °C. A second synthetic route was attempted for ethyl lactate acrylate in which ethyl lactate was reacted with acrylic acid instead of acryloyl chloride in the presence of triethylamine and the coupling agent, propylphosphonic anhydride (T3P); however, this produced a lower yield of 60% compared to 70% for the reaction with acryloyl chloride.[364,367] This second route was designed to be more sustainable by using bio-acrylic acid while T3P has reduced toxicity compared to other coupling agents. Interestingly, the thus obtained monomer was also investigated in terms of its polymerization potential. Living radical polymerization of ethyl lactate acrylate was optimized using ethanol as a green solvent with polymers ranging from DP 25 to 400 being achieved with >95% conversion and low

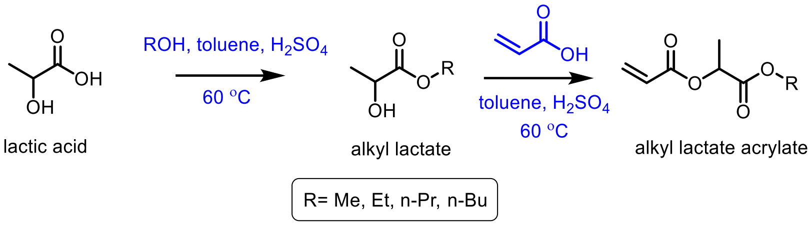


**Figure 14.** Synthesis of alkyl lactate acrylates from lactic acid *via* an alkyl lactate intermediate.

dispersities (i.e., <1.23).[364] Ethyl lactate acrylate was also copolymerized with $\alpha$-pinene acrylate and solketal acrylate to form soft-hard and amphiphilic (after deprotection) block copolymers, respectively.

Another example that coupled lactate esters with acrylic acid was conducted by Nayak and co-workers, who synthesized a series of alkyl lactate acrylates through a two-step reaction, which is summarized in Figure 14.[368] First, lactic acid was reacted with an alcohol, using sulfuric acid and toluene as the catalyst and solvent respectively to form the corresponding alkyl lactate. High yields of 94%, 92%, 91% and 95% were observed for methyl lactate, ethyl lactate, *n*-propyl lactate and *n*-butyl lactate, respectively. The second step was the reaction between the alkyl lactates and acrylic acid, again using sulfuric acid as catalyst, although the corresponding yields were slightly lower (72−93%). The resulting monomers were then successfully polymerized *via* free radical polymerization.

*3.1.3.3. From Glycerol.* Glycerol is a by-product of biodiesel production, and it is estimated 400 million tons of glycerol are produced each year. Thus, to increase the sustainability of the use of biodiesel and due to glycerol production exceeding the current demand, suitable applications need to be found for glycerol.[369] As previously discussed, glycerol can be used as a feedstock for the synthesis of acrylic and methacrylic acid. The conversion of glycerol into ketals has been thoroughly reported and these can further be used in the synthesis of different acrylate and methacrylate monomers. Goyal and co-workers combined glycerol from biodiesel with products from the ketonization of pyrolysis oil from biomass, with *p*-toluene sulfonic acid as the catalyst, to form glycerol ketals.[370] The second step was to form the methacrylate monomers which involved a transesterification of the ketal pre-monomers and methyl methacrylate, catalyzed by lipase enzymes. The resulting monomers were polymerized *via* living radical polymerization.[370] The ketal group also acts as an important protecting group during the polymerization and can be removed afterward. Yu *et al.* copolymerized solketal methacrylate, a monomer formed from the condensation of glycerol into acetone and a subsequent acrylation, with styrene.[371] It was shown that the protecting group had an effect on the polymer solution behavior as when protected, the polymer was disordered, while deprotection through hydrolysis resulted in an ordered polymer structure, as shown in Figure 15.

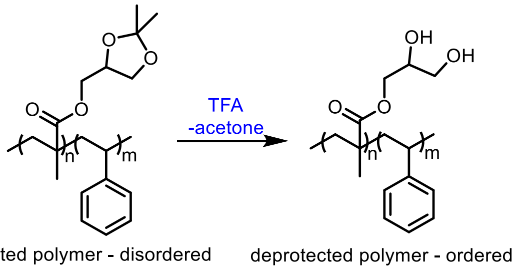


**Figure 15.** Structures of the protected and deprotected polymers and how it affects the structure of the polymer in solution.

Glycerol can be protected through a reaction with acetone and *p*-toluenesulfonic acid catalyst at 80 °C to form isopropylidene glycerol in a 73% yield.[372] This can in turn be coupled with acryloyl chloride in the presence of triethylamine.[372−377] There have been several examples of this reaction reported, with a 90% yield being the highest obtained.[376,377] The resulting monomer was also shown to be polymerized *via* copper-mediated controlled radical polymerization using a macroinitiator.[372] Polymers containing solketal acrylate (SKA) are acid-degradable and temperature responsive, while the SKA groups significantly impact the self-assembly behavior.[378−380] A hydrophobic−hydrophilic PMMA-b-PSKA block copolymer was formed by sequential addition before the hydrolysis of the solketal groups. Self-assembly of the amphiphilic polymers led to the formation of core−shell micelles with an average size of 30 nm.

*3.1.3.4. From Acrolein.* As discussed earlier in the section on acrylic acid (section 3.1.1), acrolein is an intermediate in the production of acrylic acid from glycerol and can be used in a separate process to form alkyl acrylates. For instance, gold nanoparticles have been investigated as catalysts for the production of methyl acrylate from acrolein. Kenjo and co-workers found that when an Au(2h)/MA450 catalyst was used, the optimum selectivity of MA was 78%.[381] Tsutsumi investigated the use of gold nanoparticles supported on $CeO_2$ for both the production of methyl acrylate and methyl methacrylate.[382] The morphology of the $CeO_2$ support was seen to have a major impact on catalytic performance. For the reaction of acrolein with methanol to form MA, the Au/$CeO_2$-nano performed the best, with the conversion and selectivity both >80% at low acrolein concentrations. The catalysts containing rod and cube shaped $CeO_2$ performed significantly worse, while there was a trend of decreasing catalytic performance as the concentration of acrolein increased. For the reaction of methacrolein with methanol to form methyl methacrylate, all catalysts achieved 100% selectivity, but once again it was the Au/$CeO_2$-nano that had the best catalytic performance with a conversion of 91% being obtained compared to values of 79% and 10% for the rod and cubic morphologies, respectively. In another example, Marsden and co-workers achieved a high conversion and methyl acrylate selectivity of 97% and 87% respectively for the aerobic oxidation of acrolein in methanol with a Au/ZnO catalyst at 25 °C.[383]

*3.1.3.5. From Methyl Acetate.* Methyl acrylate can further be synthesized by an aldol condensation between methyl acetate and formaldehyde in a similar reaction to that of acetic acid with formaldehyde in the synthesis of acrylic acid.[259] Methyl acetate has a lower reactivity than acetic acid and so the yields for methyl acrylate are lower than for the corresponding reaction forming acrylic acid.[384] The conversion of methyl acetate into methyl acrylate has been investigated with vanadium phosphate catalysts, showing selectivity values up to 92% with formaldehyde conversions of up to 48%.[385] The use of a cesium catalyst supported on a SBA-15 mesoporous support was explored and a methyl acetate conversion of 49% and methyl acrylate selectivity of 95% were achieved, in a reaction with a 1:2 ratio of methyl acetate to formaldehyde at 390 °C.[386] HZSM-5 catalysts doped with phosphorus and cesium have also been investigated, showing a yield of 39% and selectivity of 98%.[387]

*3.1.3.6. From Vegetable Oils and Lipids.* Vegetable oils have been used as raw materials for many different industries including in paints, coatings, biodiesel and lubricants.[388] Vegetable oils are composed of fatty acids which contains carboxylic acid and double bonds functionalities that can be used for a variety of different reactions. Examples of vegetable oils that have been studied for acrylate synthesis include soybean oil, jatropha oil, linseed oil and castor oil.[389−394] Using vegetable oils for monomer synthesis results in products containing long, and often unsaturated, hydrocarbon side chains being formed.

A particularly useful derivative for the synthesis of alkyl-substituted (meth)acrylates are fatty alcohols which can be obtained from fatty acids and esters through a catalytic hydrogenation at high temperatures and pressures. There have been a range of catalysts that have been investigated for this reaction, including Cu-based, Ru−Sn−B and Co−Sn catalysts.[395] The hydroxyl group of the fatty alcohols can then participate in an esterification reactions to form acrylate and methacrylate monomers, as illustrated in Figure 16. Pratap and co-workers carried out an esterification of various *n*-alkyl alcohols (*n* = 12−18) with acrylic acid using *p*-toluenesulfonic acid as a catalyst while Soldi and co-workers synthesized octadecyl methacrylate, tetradecyl methacrylate and hexadecyl methacrylate in 85%, 70% and 80% yield, respectively.[396,397] The enzyme Novozym 435 lipase has also been shown to work for the esterification of stearyl alcohol and oleyl alcohol.[398] The acrylate of both alcohols was formed with 65% yield, while for the methacrylate derivative, the stearyl alcohol achieved a higher yield of 94% compared to oleyl alcohol (86%). Linolenyl acrylate was formed from linolenyl alcohol through a reaction with acryloyl chloride and a yield of 65% was obtained.[399] Acrylates have also been formed from linoleyl alcohol, oleyl alcohol and lauryl alcohol, while similar approaches have been taken to form methacrylates through reactions with methacryloyl chloride.[400] However, the disadvantage of many of these procedures is that toxic acryloyl chloride and methacryloyl chloride coupling agents are required thus limiting their sustainability.

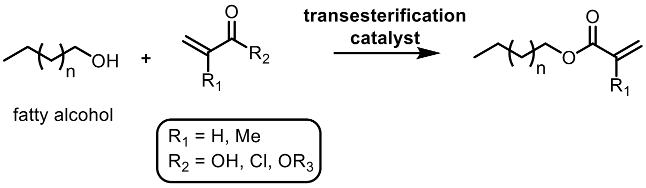


**Figure 16.** Conversion of fatty alcohols into acrylate monomers *via* an esterification reaction. $R_1$ was either H or Me while $R_2$ corresponds to either OH, Cl or $OR_3$.

There have been many previously reported approaches to synthesize acrylate and methacrylate monomers from vegetable oils which either aim to target the carbon−carbon double bond or the carboxylic acid functional group (see Figure 17 and Figure 18, respectively).[388] These methods include epoxidation-acrylation, hydroxybromination-acrylation, bromoacrylation, epoxy ring opening and transesterification.

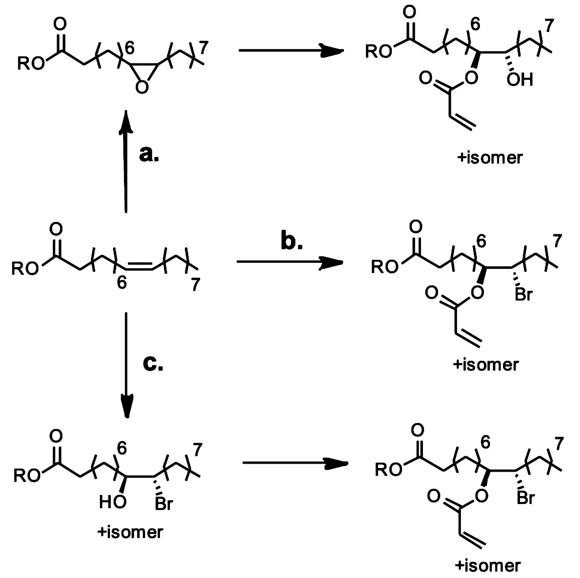


**Figure 17.** Different methods to form acrylate monomers by functionalizing the C=C bond in vegetable oils. Methods include expoxidation-acrylation (a), bromoacetoxylation (b) and hydroxy-bromination-acrylation (c).

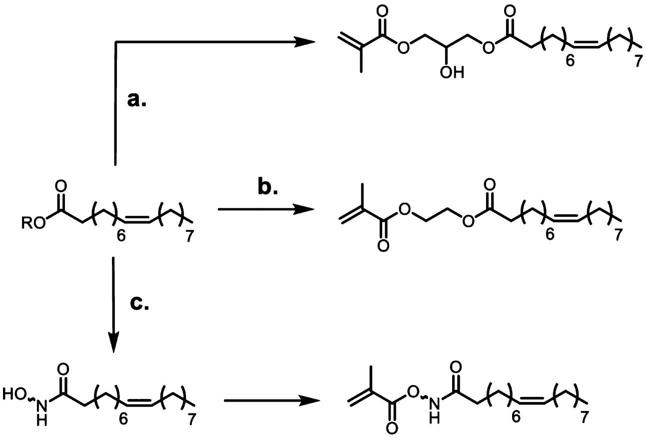


**Figure 18.** Different methods to form acrylate monomers by functionalizing the carboxylic functionality in vegetable oils. Methods include glycidyl methacrylate ring opening (a), (trans)esterification (b) and amidation-(meth)acrylation (c).

As well as synthetic routes from fatty alcohols, other routes have been proposed to functionalize fatty acids directly. One method is through an epoxidation-acrylation approach.[391,401−406] The general approach is to first convert double bonds in the fatty acid to the corresponding epoxide through reaction with peracids or peroxides in the presence of a carboxylic acid, such as formic acid.[391,401−406] The epoxy group can then be ring-opened with acrylic acid resulting in the acrylate monomer. This procedure has been carried out on

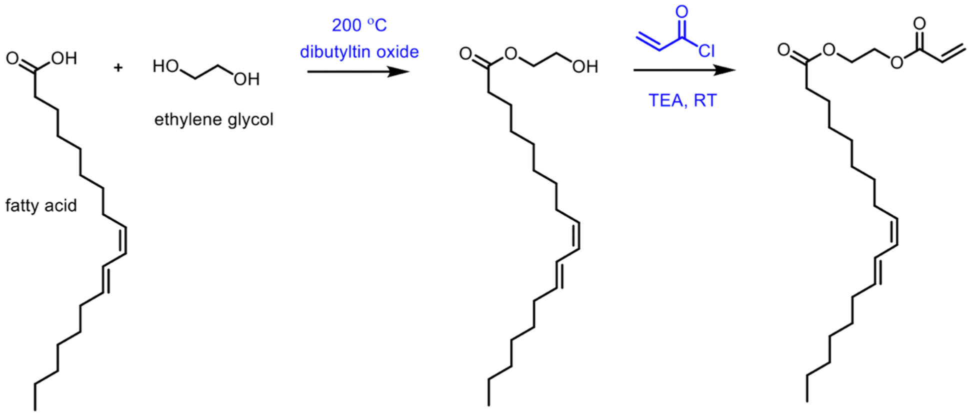


**Figure 19.** An example of an esterification between a fatty acid and ethylene glycol before a subsequent reaction with acryloyl chloride to form an acrylic monomer.

various different substrates including soybean oil and methyl oleate.[389,407−409] Huang and co-workers investigated two separate systems for the epoxidation of fatty esters.[408] The first was using formic acid and hydrogen peroxide. When using methyl oleate, methyl linoleate and methyl linolenate as the fatty esters, yields for the epoxidized products were 51%, 65% and 69%, respectively. The other system was based on a stronger acid catalyst, a mix of sulfuric acid and acetic acid. However, this setup resulted in significantly lower yields (i.e., 43%, 33% and 6% for the epoxidized products from methyl oleate, methyl linoleate and methyl linolenate, respectively). Walter *et al.* carried out the epoxidation of methyl oleate with formic acid and hydrogen peroxide at 0 °C and obtained a yield of 97%.[407] The resulting product was heated with acrylic acid for 18 h at 95 °C, resulting in the acrylated product being obtained in 86% yield. An alternative chemo-enzymatic approach to epoxidation was reported through the reaction of soybean oil and hydrogen peroxide in the presence of the enzyme CAL-B.[403] The resulting epoxidized soybean oil was acrylated through a reflux with acrylic acid.

A different approach of the carbon−carbon double bond functionalization was a hydroxybromination-acrylation method proposed by Eren and Küsefoglu.[410] The hydroxybromination of both oleic acid and methyl oleate was conducted through a reaction with a mixture of *N*-bromosuccinimide, acetone and water at room temperature for 2 h. Hence, yields of 85% and 92% were obtained for the products from methyl oleate and oleic acid, respectively. The hydroxy group on the products was then further functionalized, as in many examples, through a reaction with acryloyl chloride.

In an attempt to simplify the two-step synthetic procedures, an approach based on a simultaneous bromination and acrylation was investigated.[411] This bromoacrylation was achieved for methyl oleate by reacting it with acrylic acid and *N*-bromosuccinimide at room temperature for 1 day. A high yield of 90% was obtained, which was higher than reported for the two-step process outlined above. When repeated for soybean oil and sunflower oil, the bromoacrylation achieved yields of 75% and 55%, respectively.

As well as being able to functionalize the double bond, the carboxylic acid functionality can also be utilized to synthesis acrylic monomers. Esterification reactions between fatty acids and allylic alcohols have previously been described, but usually require a significant excess of alcohol to proceed to high conversions.[388,412,413] Therefore, alternative strategies have been investigated, including esterification. In this process, the fatty acids were heated to 55−60 °C with phosphorus trichloride for 1 h to form the acid chloride.[414] Subsequently, the product was cooled to 10 °C and allylic alcohol was added. When palmitic acid was used as the fatty acid, a yield of 78% was obtained. However, this procedure has the disadvantage of using the toxic $PCl_3$ and so an alternative route was developed, as illustrated in Figure 19. It should be noted that this procedure is mainly applicable to conjugated fatty acids. By first carrying out an efficient esterification with ethylene glycol (i.e., 92% yield) at 200 °C with a dibutyltin oxide catalyst, a hydroxyl terminated product was formed. A subsequent reaction with acryloyl chloride produced the acrylated product in 86% yield. Other synthetic routes based on esterification have been reported as well. Maiti *et al.* carried out an esterification between oleic acid and hydroxyethyl methacrylate with *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP), which resulted in a 75% yield of the methacrylate monomer.[415] Similar reactions were carried out for caprylic, capric, lauric, mysritic, palmitic and stearic acid with yields between 74%−85%.[416] The enzyme Novozym 435 has been shown to catalyze transesterification reactions of methyl methacrylate and was used to synthesize novel acrylate and methacrylate monomers from unsaturated fatty esters, with yields ranging from 65% to 94%.[388,398,417] While these methods utilize bio-based feedstock, they do not necessarily present a sustainable pathway as the use of toxic chemicals and catalysts (e.g., $PCl_3$, dibutyl tin oxide) must be considered.

Another approach to functionalize the acid group in vegetable oils, for the transformation into acrylic monomers is the amidation-methacrylation method.[418,419] The first step is the reaction of a triglyceride with an amino alcohol, such as ethanolamine at 60 °C for 4 h. Hydroxy-terminated fatty amide chains were produced with yields between 95% and 97%. A subsequent reaction with methacrylic anhydride and DMAP at 60 °C resulted in the methacrylate monomer, with almost full conversion. The second step of the reaction has also been reported using acryloyl chloride to form an acrylic version of the monomer.[420]

A final approach to acrylic monomers derived from fatty acids is through an epoxy ring-opening reaction. The general approach is the reaction of a fatty acid with glycidyl methacrylate in the presence of a catalyst.[421,422] Several catalysts have been investigated, including *N*-dimethyl benzyl amine, hexadecyl trimethylammonium chloride and benzyltriethylammonium chloride, which obtained high yields of 94%, 94% and 91%, respectively.[423] Two catalysts were used for the reaction of oleic acid with glycidyl methacrylate, to form a methacrylate monomer.[424−426] One approach used a chromium(III) based catalyst (AMC-2) at 80 °C while the second featured a zinc based catalyst (Nacure XC-9206) being used at 100 °C. The resulting monomer was polymerized through free radical mini-emulsion polymerization, while the double bond from the oleic acid can be used as a cross-linking unit in gel formation.[424] The monomer was also copolymerized with $\alpha$-methylene-$\gamma$-butyrolactone in a mini-emulsion polymerization, forming renewable polymer latexes with tunable properties.[425]

There have been many examples of acrylates and methacrylates derived from vegetable oil/fatty acids being polymerized. To investigate potential bio-based adhesives, Badia and co-workers for instance carried out an emulsion polymerization of 2-octyl acrylate, derived from castor oil, and isobornyl methacrylate, derived from pine resin.[394] Soybean oil contains many unsaturated double bonds within the structure; however, they are usually unreactive and need to be converted into other functional groups, such as epoxides, to increase their reactivity.[427] Epoxy groups can be incorporated into the structure of soybean oil through the reaction of double bonds with hydrogen peroxide in the presence of acetic or formic acid.

**3.1.4. Cyclic (Meth)acrylate.** *3.1.4.1. From Terpenes.* Another potential bio-source for (meth)acrylate monomers are terpenes and terpenoids (Figure 20), which can be derived from biomass including wood ($\alpha$-pinene and $\beta$-pinene) or citrus (limonene).[428] While terpenes contain vinyl groups and are based on isoprene $C_5H_8$ units, terpenoids (e.g. menthol and carvone) are derived from terpenes and contain additional functional groups. The homopolymerization of the vinyl groups of terpenes proved unsuccessful through free radical polymerization,[429] although when copolymerized with styrenics or acrylates, low molecular weight polymers were obtained.[430]

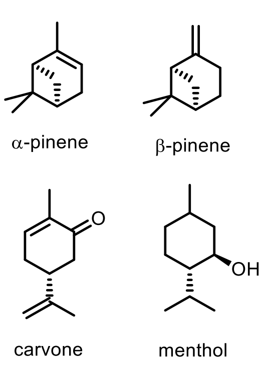


**Figure 20.** Structures of different terpenes and terpenoids that have been used to synthesize acrylate monomers.

Sainz and co-workers transformed (+)-$\alpha$-pinene, (−)-$\beta$-pinene, (*R*)-(+)-limonene and (*R*)-(−)-carvone into acrylates and methacrylates *via* a two-step approach.[428] The first step was to convert the terpenes into alcohols before esterification with the relevant acryloyl or methacryloyl chloride. For $\alpha$-pinene, $\beta$-pinene and limonene, the first step consisted of a hydroboration/oxidation step.[428,431,432] For limonene, a hindered borane was used to selectively react with the less hindered vinyl group. The first step for the carvone synthesis was different due to the presence of a ketone group, which was reduced with $LiAlH_4$ to form the corresponding alcohol.[428,433] The formations of the alcohols proceeded with high yields (>82%, see Figure 21).

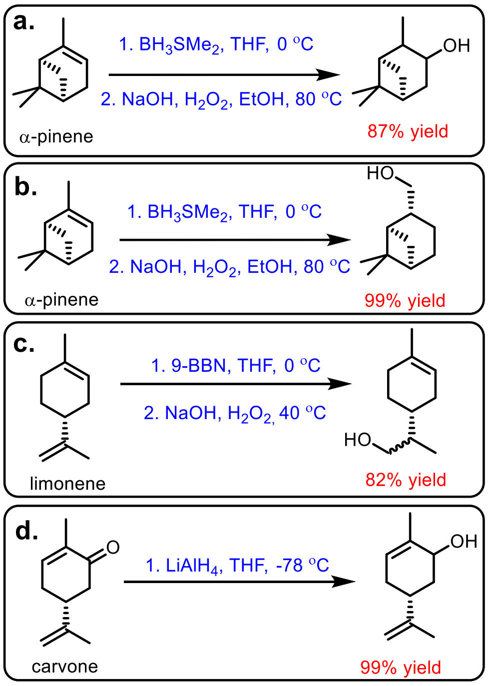


**Figure 21.** Reaction schemes to form hydroxy-functionalized terpenes/terpenoids, which were then reacted further to form acrylic monomers.

With the terpene-based alcohols available, several different methods were then employed to synthesize the actual acrylate/methacrylate monomers, as exemplified for (+)-$\alpha$-pinene in Figure 22 and Figure 23.[428] As previously described, the reaction of alcohols with acryloyl or methacryloyl chloride is typically used to synthesize acrylates and methacrylates. However, in a bid to remove the use of acryloyl or methacryloyl chloride so to produce a more sustainable method, esterification with acrylic and methacrylic acid presents a desirable alternative. This was achieved by using propyl phosphonic anhydride (T3P) as the coupling agent, with higher yields achieved for the acrylate monomers than for the synthesis with acryloyl chlorides.[367,428] However, no yields were reported for the synthesis of methacrylates using T3P. Sainz et al. also developed a new one pot synthesis built on White's catalytic allylic oxidation, which uses a $Pd(OAc)_2$ catalyst to oxidize the allylic position of $\beta$-pinene (Figure 24).[428,434] Conditions were screened and optimized, indicating the use of 2 mol % $Pd(OAc)_2$, 2 equiv of benzoquinone at 50 °C for 72 h to yield two new monomers with 82% yield.

Another (meth)acrylate monomer, derived from the monoterpenoid menthol, that is receiving increased attention is menthyl acrylate.[364,435−440] Unlike the aforementioned terpenes, menthol has a hydroxy functional group available on the scaffold and so the acrylic monomer can be formed in a one-step synthesis upon the addition of acryloyl or methacryloyl chloride. Indeed, Baek and co-workers synthesized menthyl acrylate by reacting menthol with acryloyl chloride with a yield of 73%.[439] The monomer was shown to

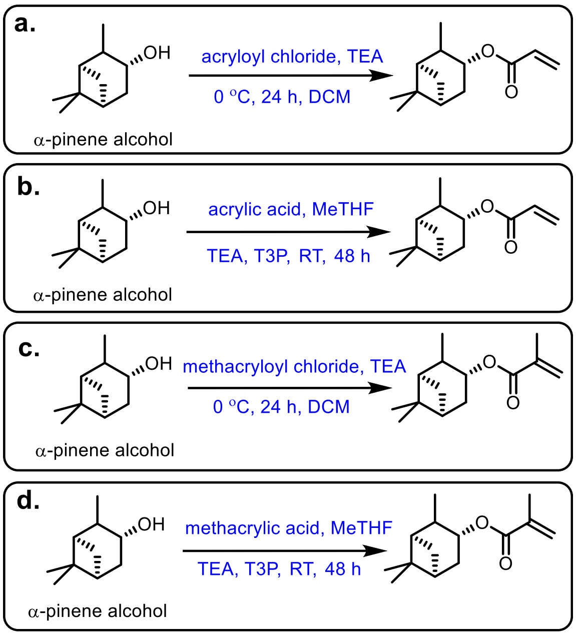


**Figure 22.** Different approaches to form acrylic and methacrylic monomers from $\alpha$-pinene alcohol.

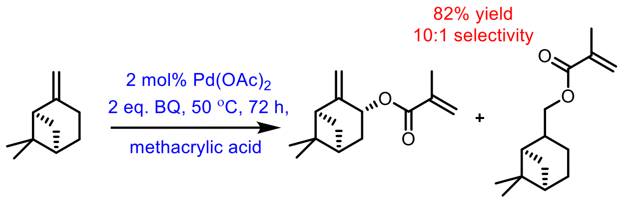


**Figure 24.** Scheme for the White's allylic oxidation of $\beta$-pinene.

be co-polymerized with 2-ethylhexyl acrylate and 2-hydroxyethyl acrylate in a UV-initiated bulk process to form a pressure sensitive adhesive. Additionally, Argyros and co-workers synthesized menthyl methacrylate in 56% yield using methacryloyl chloride, which could be copolymerized with MMA *via* free radical polymerization, both in bulk and solution.[438] Notably, the chirality of the menthol starting material was the focus of their work in exploring the feasibility in polymer optic fiber applications. As well as free radical polymerization, the living radical polymerization of menthyl acrylate and menthyl methacrylate has been heavily explored.[364,435,436,440]

Another (meth)acrylate monomer that has been explored is derived from sobrerol, for which different synthetic approaches have been taken (Figure 25).[441,442] Similar to menthol, sobrerol contains a hydroxy functional group and is synthesized through the hydration of $\alpha$-pinene oxide.[442] The synthesis of sobrerol acrylate was completed by reacting sobrerol with acryloyl chloride with a yield of 72% being obtained. The synthesis of the sobrerol methacrylate derivative achieved a yield of 84% and was carried out by treating sobrerol with methacrylic anhydride in the presence of DMAP at 50 °C. Both monomers have been investigated for their potential use to replace styrene in unsaturated polyester resins (UPRs).[442] Additionally, Stamm and co-workers investigated other potential routes to synthesize sobrerol methacrylate as

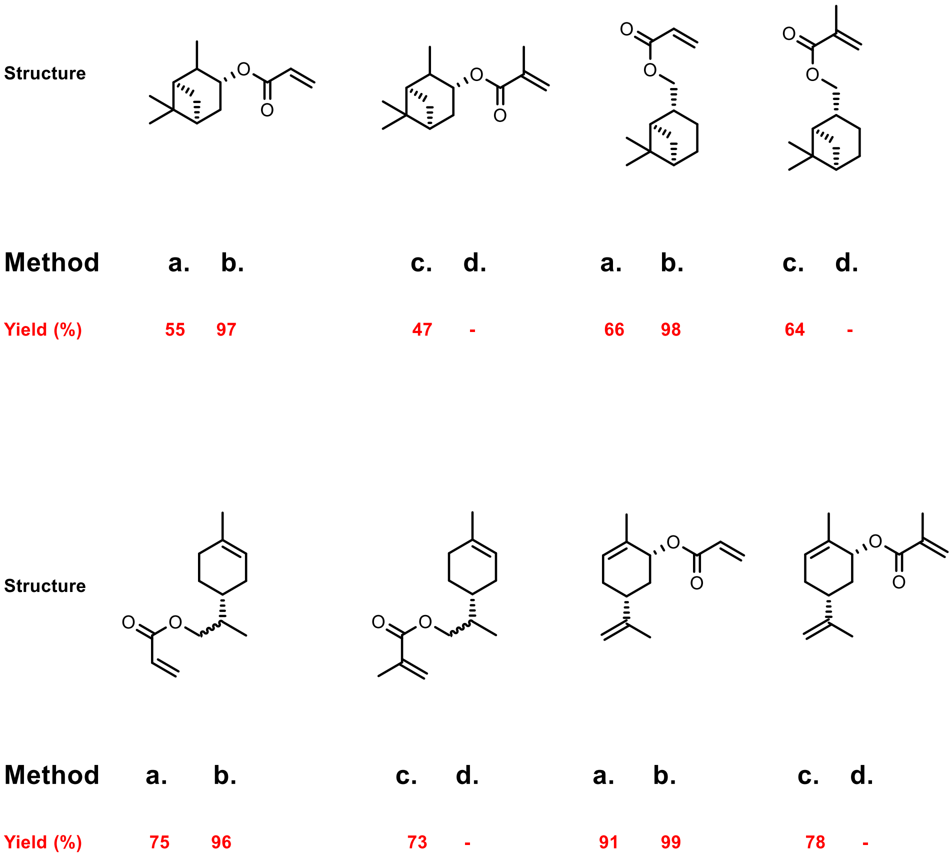


**Figure 23.** Reported yields for the acrylic and methacrylic monomers derived from terpenes *via* four different methods.

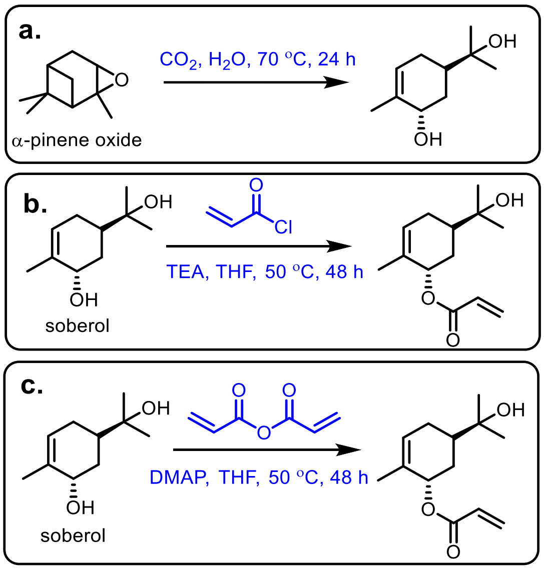


**Figure 25.** Schemes for the formation of sobrerol from α-pinene oxide (a), the acrylation of sobrerol with acryloyl chloride (b) and the methacrylation of soberol with methacrylic anhydride and DMAP (c).

shown in Figure 26.[441] First, α-pinene was converted into sobrerol, catalyzed by cytochrome P450-BM3/2M monooxygenase from *Bacillus megaterium*. *Trans*-sobrerol was also shown to be the main product from the biotransformation of (+)-α-pinene with *Armillariella mellea*.[443] Sobrerol methacrylate was then derived from its corresponding alcohol *via* two routes.[441] The first was a conventional esterification with methacryloyl chloride with a yield of 66% being reached. The second route was a greener approach that used vinyl methacrylate and the amino lipase enzyme originating from pseudomonas fluorescens, with the enzymatic approach giving a much higher conversion (i.e., 96%) than the chemical synthesis pathway. The resulting monomer was successfully used in conventional living radical polymerizations and also copolymerizations with MMA and BMA were conducted.

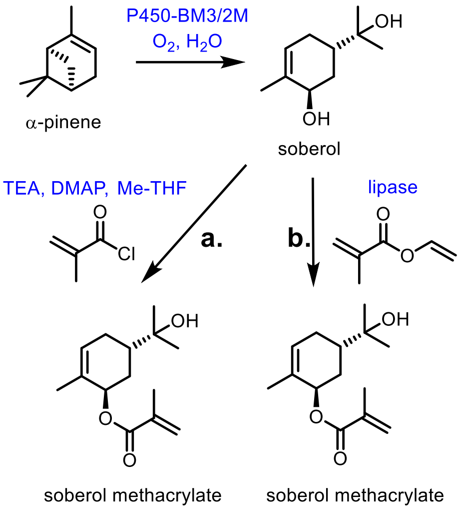


**Figure 26.** Two different routes to synthesize sobrerol methacrylate from α-pinene. The second step was conducted *via* a chemical route (a) and biochemical approach (b).

*3.1.4.2. From Isosorbide.* Isosorbide is considered one of the top 12 most renewable building blocks and is a chiral bicyclic diol, derived from glucose (Figure 27).[444] There have been many potential applications of isosorbide which include monomer synthesis, being used as a bio-based organic solvent, or for use in the pharmaceutical/medical fields.[445] As well as being a sustainable bio-source, isosorbide also has other advantageous properties as it brings rigidity, thermal stability, and is also considered to be non-toxic. As an example, the oxygen barrier and mechanical properties of poly(butylene succinate) could be improved when the rigid isosorbide was incorporated into the structure, while the non-toxicity of isosorbide allowed for it to be used as a substitute for bisphenol A in epoxy resins and polycarbonates.[445−447]

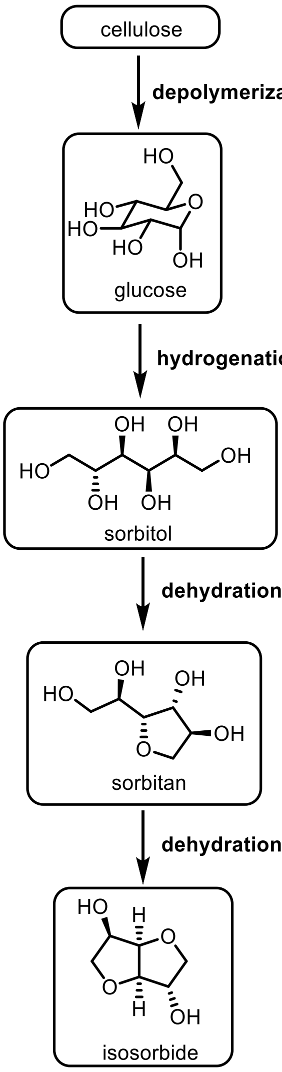


**Figure 27.** Synthetic route of isosorbide from glucose.

Isosorbide can be synthesized from starch through chemical-biological processes, which include enzymatic hydrolysis to form glucose followed by a hydrogenation to sorbitol before a final dehydration step.[445,446,448] This hydrogenation to sorbitol can be performed through well-established synthetic procedures.[448−450] The double dehydration of sorbitol is the major step in the synthesis of isosorbide, and problems including chemo- and regioselectivity and the formation of side products have to be overcome.[448] There have been many different homogenous and heterogeneous catalysts that have been used for this crucial step in the synthesis. For instance, the dehydration step has been catalyzed by strong Bronsted acids (e.g., hydrochloric and sulfuric acid) in order to transform one of the hydroxy groups into a good leaving group.[448,451,452] Lewis acids have also been used to catalyze this reaction with metal triflates (e.g., bismuth(III)triflate and gallium(III)triflate) proving better results than metal chlorides (e.g., $AlCl_3$ and $SnCl_4$) and sulfuric acid.[448,453−455] Acid-free conditions have also been applied when water was used as a solvent at high temperatures, as the self-ionization of water promoted the dehydration reaction.[448,456,457] Heterogeneous catalysts that have been used include acid resins zeolites, metal oxides, metal phosphates and tungsten phosphoric acids supported on metal oxides.[448,458−463] A one-pot synthesis of isosorbide was investigated by developing a hydrogenation catalyst containing acid. In this case, a heterogeneous bifunctional catalyst was used that contained 0.2 wt % of ruthenium on a Bronsted acid support with an optimized yield of 85%.[464] De Almeida *et al.* carried out the synthesis of isosorbide from cellulose in a molten $ZnCl_2$ medium.[465] The $ZnCl_2$ was found important in dissolving and hydrolyzing the cellulose into glucose, before a ruthenium catalyst was used for the hydrogenation step. The dehydration step was found to proceed both in the plain molten $ZnCl_2$ medium, or in the presence of $CuCl_2$ or $NiCl_2$ catalysts.

Once synthesized, isosorbide can then be functionalized into monomers such as acrylates and methacrylates. Due to isosorbide containing two hydroxy functionalities, carefully planned synthetic procedures must be carried out to obtain a mono-functional monomer. Imanzadeh and co-workers synthesized a mono-functional isosorbide methacrylate by using orthogonal protecting groups.[466] The synthesis is shown in Figure 28, and an overall yield of 23% was obtained. First, selective mono-acetylation of isosorbide was conducted before the remaining hydroxy group was protected with a tetrahydropyran group.[467] The acetyl group was removed *via* basic hydrolysis before further reacting with methacryloyl chloride. The final step was to remove the tetrahydropyran protecting group using pyridinium *p*-toluenesulfonate in methanol. Gallagher and co-workers synthesized both acetylated isosorbide methacrylate (AMI) and acetylated isosorbide acrylate (AAI) (Figure 29).[468] AMI was prepared through a mono-acetylation, followed by a further reaction with methacrylic anhydride and a scandium(III) triflate catalyst. The second step reached full conversion after 4 h with 1 mol % catalyst, while the overall yield for the synthesis was reported to be 44%. The resulting monomer was polymerized through free radical polymerization to form a high $T_g$ polymer ($T_g$ = 130 °C), while also a block copolymer of the acetylated isosorbide methacrylate and butyl acrylate has been successfully achieved. The AAI monomer was formed by reacting the acetylated intermediate with acryloyl chloride.[469] The yield of the acetylation was recorded as 38%, while the reaction with acryloyl chloride achieved a 58% yield. The resulting monomer was used to form a PAAI−PBA-PAAI triblock, which showed good mechanical properties for potential use as pressure sensitive adhesives.

As well as examples utilizing protecting groups, other routes to monofunctional (meth)acrylates synthesized from isosorbide make use of the difference in reactivities between the exo- and endo- hydroxy groups. Baek *et al.* synthesized a mono-functional isosorbide acrylate using acryloyl chloride, selectively producing the endo-isomer with 35% yield.[470] The resulting monomer was co-polymerized with 2-ethylhexyl acrylate and 2-hydroxyethyl acrylate for potential use in pressure-sensitive adhesives. Biochemical routes to synthesize monomers derived from isosorbide have also been developed. For example, Matt and co-workers synthesized mono-functional isosorbide methacrylate *via* two methods, which both used a lipozyme RM IM (*Rhizomucor miehei* lipase) catalyst (Figure 30).[471] One method, using vinyl methacrylate, achieved a yield of 87% and >99% selectivity for the endo-isomer. The other method, which used methacrylic anhydride achieved a lower yield of 75%, but showed a similar selectivity for the endo-isomer. The monomer was shown to be susceptible to free radical polymerization, obtaining a polymer with a high $T_g$ of 167 °C. The advantages of these biochemical methods is its one-step process, rather than a multi-step synthesis that resulted in a higher overall yield, as well as eradicating the use of metal catalysts.

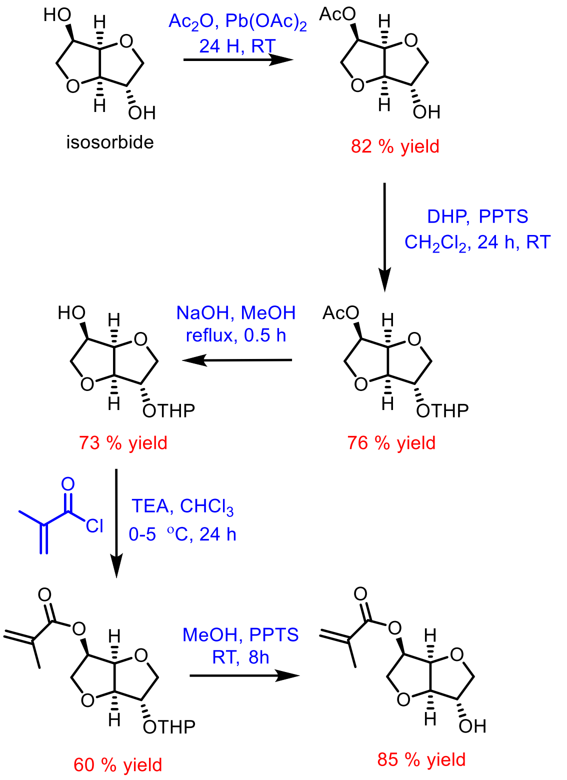


**Figure 28.** Synthesis of a mono-functional acrylate from isosorbide utilizing orthogonal protecting groups.

Due to isosorbide containing two hydroxy groups, there is also the potential to synthesize bifunctional monomers besides only mono-functional derivatives.[444,472−475] Indeed, Liu *et al.* synthesized a rigid isosorbide methacrylate bifunctional monomer, using a solvent free approach, by reacting isosorbide with methacrylic anhydride at 60 °C using ultrasonication.[444] The methacrylic anhydride to isosorbide ratio was optimized at 3:1, resulting in a high yield of 92%. The resulting monomer was copolymerized with acrylated epoxidized soybean oil to form a bio-based thermoset resin. It was shown that this bio-based resin had lower viscosity and curing temperature and higher polymerization rates, while the combination of the rigid isosorbide methacrylate and flexible soybean oil derivative resulted in enhanced mechanical and thermal properties. Badia and co-workers synthesized a mixture of mono- and bi-

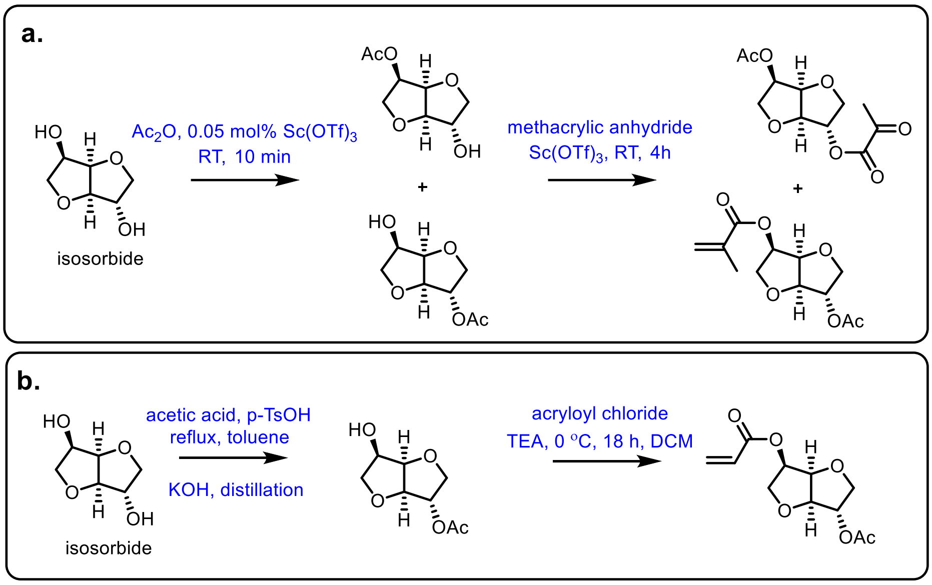


**Figure 29.** Synthesis of acetylated isosorbide methacrylate (a) and acetylated isosorbide acrylate (b).

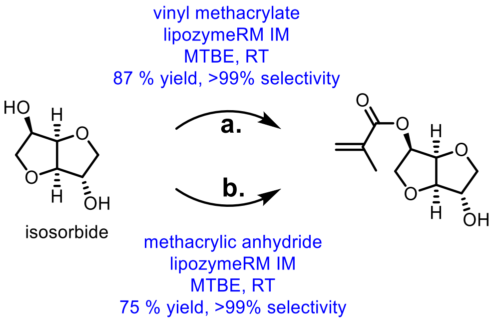


**Figure 30.** Biochemical approaches to synthesize a monofunctional isosorbide methacrylate.

functional isosorbide methacrylate monomers by reacting isosorbide with methacrylic anhydride with a yield of 56% being obtained.[472,474] The resulting mixture contained an 8:2 ratio of mono- to bi-functional monomer, from which the mono-functional methacrylate was separated *via* column chromatography (35% yield). In a final example, Howell and co-workers synthesized diphenylphosphato acrylates from isosorbide in a two-step reaction (Figure 31).[473] Specifically, isosorbide was reacted with diphenylchlorophosphate and triethylamine at 0 °C, forming two isomers which were separated *via* column chromatography. Each isomer was then treated with acryloyl chloride to form the corresponding acrylate monomers. The endo- and exo-acrylate monomers were obtained in high yields of 98% and 93%, respectively.

*3.1.4.3. From Lactones.* Lactones are cyclic esters that can be polymerized *via* ring-opening polymerization (cf. section 4.1). Some lactones possess a vinyl group and can be regarded as cyclic acrylates (Figure 32). An example is $\alpha$-methylene-$\gamma$-butyrolactones (MBL), which is an important bio-source found in tulips, and is represented in about 10% of known natural products.[476−479] Such a wide use originates from its biological, cytotoxic anti-cancer and antimicrobial properties.[478,480,481] MBL is a more reactive cyclic analogue of methyl methacrylate, with the increased reactivity attributed to the relief of ring strain driving the polymerization reaction.[482] Thus, MBL is an acrylate which can be polymerized *via* free radical polymerization, as illustrated by the formation of a homopolymer with a high $T_g$ of 195 °C.[482] As well as MBL, other lactones have been converted into acrylate monomers.

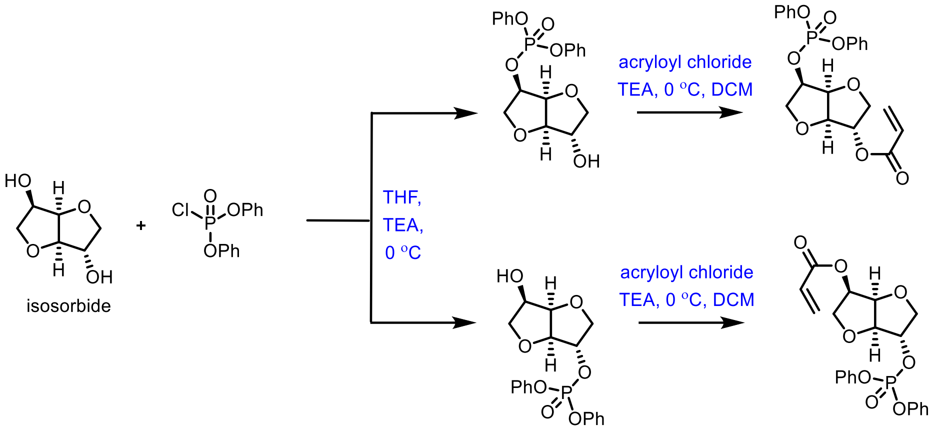


**Figure 31.** Conversion of isosorbide into two isomers of diphenylphosphato acrylates.

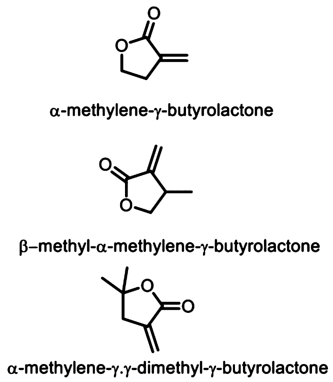


**Figure 32.** Butyrolactone derivatives also known as cyclic acrylates.

While MBL can be obtained naturally from tulips, this is an expensive process and so more viable sustainable routes have been investigated.[483] One of these uses itaconic acid as the starting material to form a *β*-monomethyl itaconate ester, derived from an itaconic anhydride intermediate, which can be reduced to the alcohol using $LiBH_4$.[483,484] The latter then undergoes an acid catalyzed cyclization to form the 5-membered lactone (49% yield from *β*-monomethyl itaconate).[483,485]

Two synthetic routes to *β*-methyl-*α*-methylene-*γ*-butyrolactone (MMBL) from the sugar-based itaconic acid were devised by Gowda and co-workers (Figure 33).[486] The first route consisted of 3 steps (Figure 33a), with the first stage being a reduction of itaconic acid with 100 bar $H_2$ at 195 °C using a ruthenium(III) acetylacetonate catalyst and diphosphine ligand. A pair of isomers and a side product were produced with the ratio of the desired to undesired isomer being 1:1.15. The mixture of isomers was reacted with diethyl oxalate and sodium methoxide before the resulting sodium salt was reacted with potassium carbonate and aqueous formaldehyde in *tert*-butylmethyl ether to give the desired product with an overall yield of 15%.[486−488] The second, six-step, route was designed to be greener and to improve the overall yield of the synthesis (Figure 33b). Here, the first step was a partial esterification of itaconic acid with methanol using acetyl chloride as a catalyst to form a monomethyl ester.[486,489,490] This was followed by a catalytic hydrogen transfer reduction with a Pd/C catalyst and ammonium formate as the hydrogen source.[486,491,492] Then, the remaining carboxylic acid was reduced to the primary alcohol using $BH_3.SMe_2$ before a distillation containing a catalytic amount of *p*TsOH. It is noteworthy that this step selectively gives the desired isomer, which the reduction in the former synthetic route failed to achieve. The second and third steps from the first synthesis were then repeated to form the desired product with an increased overall yield of 53%. While this second route, despite being longer, is a significant improvement on the first, neither procedures can be considered highly sustainable, primarily due to the nature of the used chemicals. Nonetheless, the resulting monomer was successfully polymerized *via* organocatalytic conjugate addition polymerization, demonstrating its potential use in polymer science.[486,493,494]

Trotta and co-workers derived a single-step synthesis of another lactone, *α*-methylene-*γ*,*γ*-dimethyl-*γ*-butyrolactone ($Me_2MBL$), which was successfully synthesized from *β*-monomethyl itaconate through a single-step reaction with the Grignard reagent MeMgCl, obtaining yields up to 55%.[485]

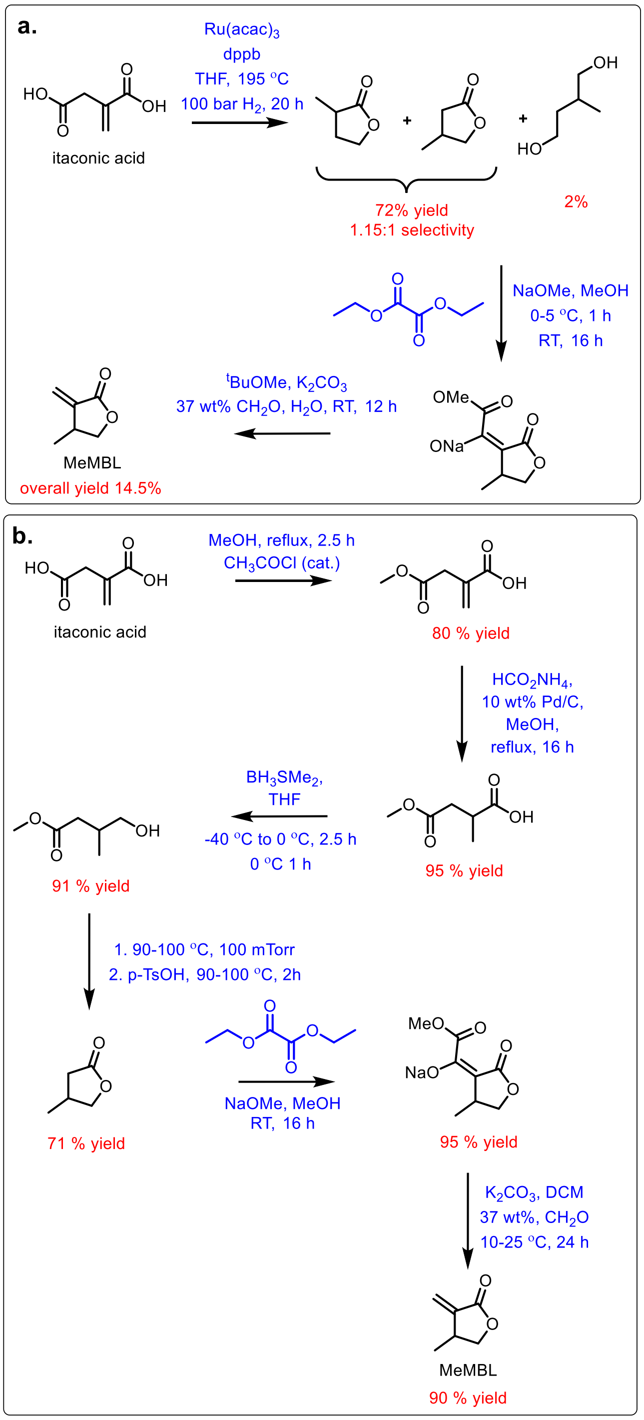


**Figure 33.** Two routes to form *β*-methyl-*α*-methylene-*γ*-butyrolactone (MMBL).

Another single step synthesis using the same starting material was derived using $NaBH_4$ rather than the Grignard reagent, to form MBL in an optimized yield of 56%. The monomers were successfully converted into polymers with a range of molecular weights and narrow dispersity. Homopolymers of MBL and copolymers containing MBL and MMA have also been prepared *via* Cu-mediated controlled radical polymerization techniques, obtaining polymers with molecular weights ranging from 31 800 to 62 400 g $mol^{-1}$.[476,495] Zhang *et al.* polymerized MBL using $Al(C_6F_5)_3$ catalysts and obtained a 91% yield and a molecular weight of 44 800 g $mol^{-1}$. When MMBL was polymerized using the same catalyst, the reaction proceeded to full conversion obtaining a 192 000 g mol$^{-1}$ polymer.[479]

*3.1.4.4. From Levoglucosenone.* Levoglucosenone is a sugar enone with a cyclic structure containing a double bond and can be easily modified.[496] It is a valuable chiral molecule that is obtained from cellulose *via* flash pyrolysis.[497,498] An advantage of using levoglucosenone over other bio-sources is that it can be produced from the pyrolysis of cellulose-containing industrial materials, for example waste paper.[499] It is an important chiral precursor to many compounds including natural products, anticancer drugs, and green solvents. The production of levoglucosenone shows increased selectivity when an acid catalyst, such as phosphoric acid, solid superacids or zeolites, is used in the pyrolysis process.[499−502] Cyrene is the reduced form of levoglucosenone and has the potential to be used as a green solvent.[497,503,504]

The Baeyer−Villiger oxidation of levoglucosenone and Cyrene results into the formation of two lactones: 5-hydroxy-2-penten-4-olide (HBO) and dihydro-5-hydroxyl furan-2-one (2H-HBO) (Figure 34), which can then be used for acrylate monomer synthesis.[365,505] The products from the above synthesis, HBO and 2H-HBO, both contain hydroxyl functional groups. As for previous examples, including those derived from terpenes and isosorbide, these hydroxyl groups can be readily converted into acrylate or methacrylate groups (Figure 35). The two main methods for the synthesis were again the reactions of the feedstock with either methacryloyl chloride or methacrylic anyhydride. Specifically, Zamzow *et al.* synthesized 2H-HBO methacrylate in 61% yield by reacting 2H-HBO with methacryloyl chloride (Figure 35a),[506] while Ray and co-workers prepared the same monomer achieving a yield of 79% using methacrylic anhydride as a substitute for the more hazardous methacryloyl chloride (Figure 35b).[496] Again, free radical polymerizations of the resulting monomer was successfully demonstrated. In another method, Allais and co-workers developed the synthesis of 2H-HBO methacrylate from 2H-HBO, which in turn can be derived from the levoglucosenone.[507] Levoglucosenone was first converted to HBO using the lipase CAL-B and hydrogen peroxide, before the resulting product underwent hydrogenation into 2H-HBO. The conversion into the methacrylate monomer was carried out by the transesterification reaction of the resulting 2H-HBO with methyl methacrylate, using a catalytic amount of CAL-B, resulting in a yield of 62% (Figure 35c). The monomer was successfully polymerized, forming both homopolymers and co-polymers with methacrylamides. Previously, Warwel *et al.* showed that also an enzyme, Novozym-435, from the lipase *Candida antarctica*, could be used to catalyze the trans-esterification of methacrylates.[398] A final approach to levoglucosenone-derived acrylics by-passed the synthesis of 2H-HBO from Cyrene and instead focused on the direct synthesis of methacrylated Cyrene *via* a two-step reaction (Figure 35d).[508] The first step was the high yielding (i.e., 95%) reduction of the ketone functionality with $LiAlH_4$, followed by the addition of methacrylic anhydride in the presence of a base to form the monomer with 86% yield. The resulting monomer was successfully polymerized in bulk, emulsion and solution.

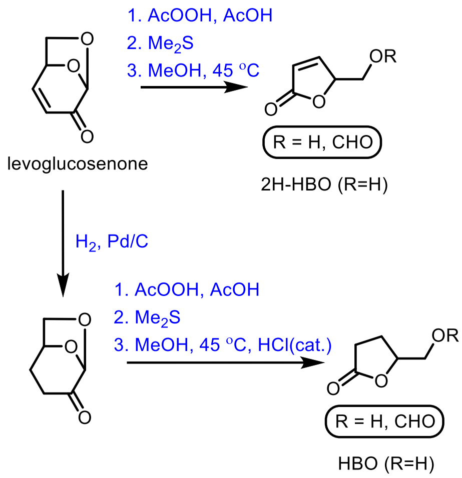


**Figure 34.** Synthesis of HBO and 2H-HBO, which were intermediates of the synthesis of acrylic monomers from levoglucosenone.

**3.1.5. Aromatic (Meth)acrylates.** Due to aromatic groups offering high stability, rigidity, and hydrophobicity for polymer chains and being predominantly petroleum based, interest in renewable aromatic polymers has greatly increased in recent years.[509] The main source of aromatic biomass comes from lignin, representing 15-30% of lignocellulosic biomass.[365,510] While lignin is difficult to process, (meth)acrylate monomers can be conveniently formed by reacting hydroxyl-containing bio-aromatic compounds derived from lignin.[22,365] These monomers can then be polymerized to form high $T_g$ polymers, which are of interest as potential styrene mimics. However, it is noteworthy that as these structures differ significantly from the structure of styrene, their ability to act as a direct replacement for styrene is limited. The structures of the key aromatic platform chemicals derived from lignin and used to synthesize bio-based acrylics are shown in Figure 36 and include vanillin, guaiacol, syringol and eugenol.[365,511]

One of the most widely used platform chemicals derived from lignin is vanillin. Vanillin can be formed from lignin by many different processes including the pulping of kraft lignin, lignin depolymerization, bisulfitation of lignin and lignin alkaline oxidation.[510,512−514] Other phenolic compounds, such as guaiacol, syringol and their derivatives, can be derived from lignin through similar processing.[515,516] Once these key feedstock chemicals have been derived from lignin, many examples have been reported for their transformation into methacrylate or acrylate-containing monomers. Many of these monomers have then been polymerized in an effort to replicate the properties of the non-bio-based alternatives (e.g., polystyrene). Two main methods have been reported for the synthesis of bio-based (meth)acrylates from lignin derivatives. Of reported examples, the methacrylating agent is either methacrylic anhydride or methacryloyl chloride, while the acylates were formed with acryloyl chloride. These two synthetic methods, as well as the synthesis of a bi-functional monomer, are illustrated in Figure 37 for vanillin and are more broadly applicable to other lignin-based platform chemicals.

Several different compounds originating from lignin have been converted into (meth)acrylates and then polymerized. In 2012, Wool and co-workers synthesized methacrylated vanillin by reacting vanillin with methacrylic anhydride with a DMAP catalyst at 50 °C for at least 24 h.[517] This bio-monomer was then cured with a glycerol dimethacrylate cross-linker to form a thermoset resin. A glass transition temperature of 155 °C was recorded, which is comparable with commercially available non-bio-based vinyl ester resins. Holmberg and co-workers synthesized vanillin methacrylate using the same reaction

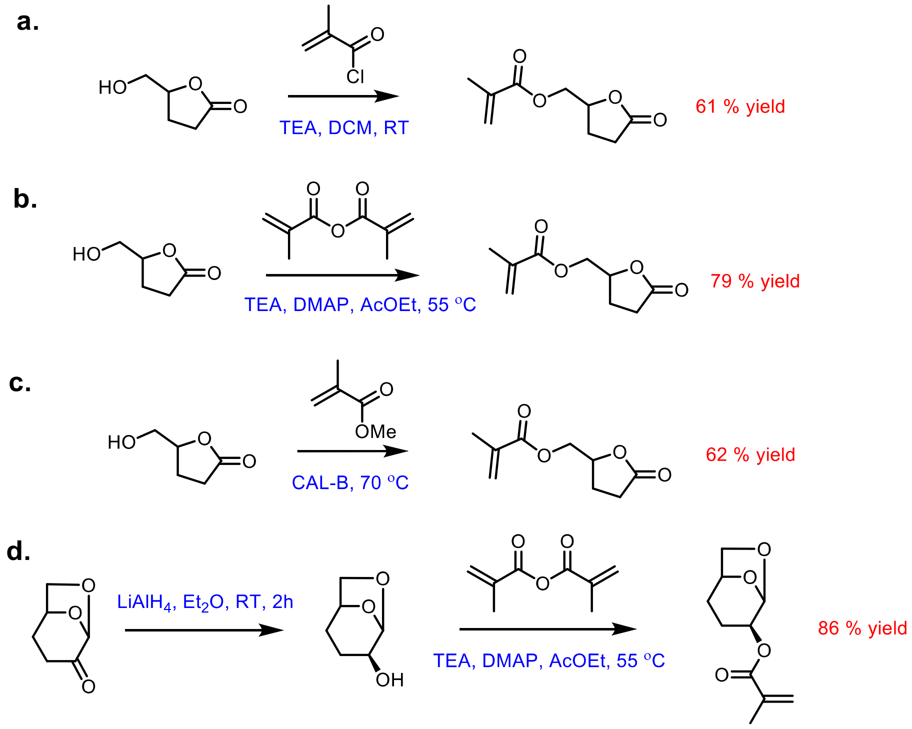


**Figure 35.** Different routes to form methacrylates from 2H-HBO and Cyrene.

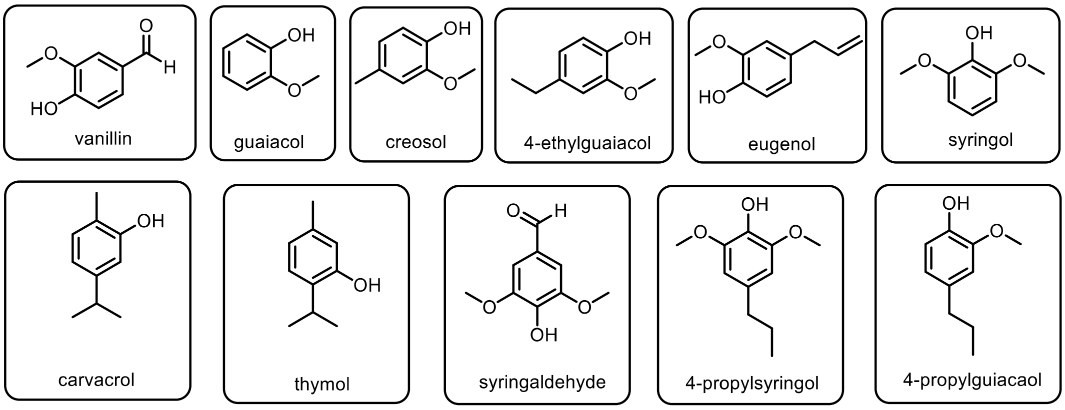


**Figure 36.** Structures of different platform chemicals derived from lignin.

conditions and utilized it in a co-polymerization with lauryl methacrylate.[518] In addition to vanillin methacrylate, Epps and co-workers further synthesized guaiacol methacrylate, creosol methacrylate and 4-ethylguaiacol methacrylate *via* the same method, before the kinetics and reactivity ratios of their polymerizations were screened.[519] Guaiacol methacrylate, creosol methacrylate, 4-ethylguaiacol methacrylate have also been obtained by reacting the corresponding lignin derived bio-precursors with methacrylic anhydride.[520] The properties of the resulting homopolymers were also investigated, showing slightly higher $T_g$ polymers were observed for poly(vanillin methacrylate) and poly(cresol methacrylate) (132−139 °C) compared to poly(guaiacol methacrylate) and poly(4-ethylguaiacol methacrylate) (116−120 °C). In a separate study, similar reactions were also conducted for the synthesis of methacrylated guaiacol and methacrylated eugenol.[521] The homopolymers of methacrylated guaiacol and methacrylated eugenol had $T_g$ values of 92 and 103 °C, respectively, and when blended with standard ester resins, the glass transition temperatures were comparable to styrene-ester resin blends. Syringyl methacrylate was also synthesized, although with a very poor yield of 7 wt %, albeit >99% in purity.[522] Unlike the previous lignin-derived compounds, syringyl methacrylate, synthesized from syringol, is classified as originating from hardwood lignin. The resulting monomer has a remarkably high $T_g$ for amorphous, linear, aliphatic polymers (i.e., 185−205 °C depending on molecular weight) and it has the potential to increase the $T_g$ and mechanical resistance of copolymers, with only small amounts added.

Apart from monomers, a bi-functional vanillin methacryate has also been synthesized, by first carrying out a reduction of the aldehyde, before the reaction with methacrylic anhydride.[523] The reduction can be carried out using reducing agents such as $LiAlH_4$ or $NaBH_4$, before the resulting vanillyl alcohol can undergo a reaction with methacrylic anhydride with DMAP at 50 °C for 18 h. The bifunctional methacrylated vanillyl alcohol was effectively used as a cross-linker in a bulk polymerization, with the resulting resin reported to show

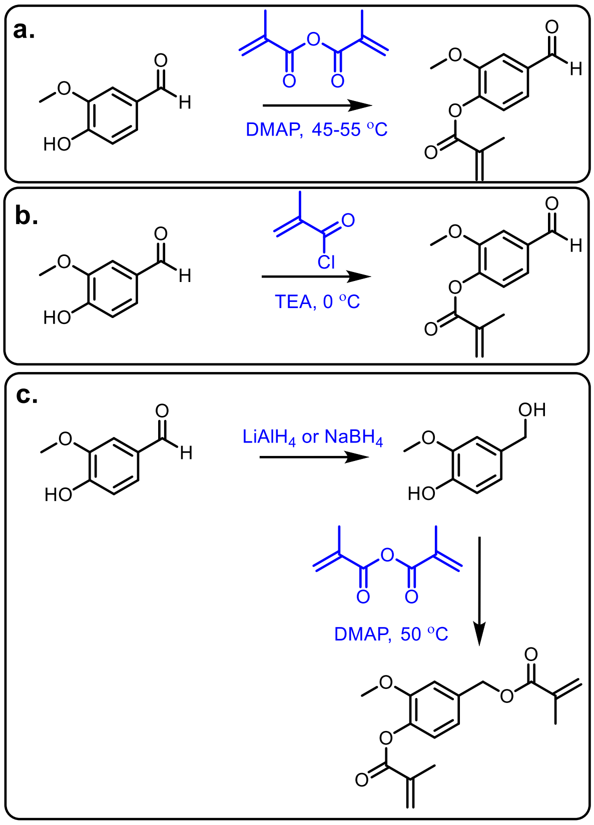


**Figure 37.** Synthetic routes to vanillin methacrylate by using methacrylic anhydride (a) and methacryloyl chloride (b). The synthesis of a bifunctional methacrylate is also shown (c).

improved mechanical properties compared to the resin formed with the monofunctional vanillin methacrylate.

Aromatic chemicals derived from plant oils, such as thymol, can also be used to synthesize acrylic monomers to investigate their use as potential as styrene replacements.[524] Due to these monomers sharing the same aromatic nature of styrene, there is potential to replace petroleum derived styrene with these bio-based monomers. Vergara *et al.* synthesized three monomers derived from carvacrol (oregano), thymol (thyme) and menthol (mint). The monomers derived from carvacrol and thymol were aromatic, while the monomer from menthol has a non-aromatic cyclic structure. The three monomers were synthesized by reacting the bio-source with methacrylic anhydride with a DMAP catalyst at room temperature for 24 h. Yields of 78%, 77% and 73% were obtained for caracryl methacrylate, thymyl methacrylate and menthyl methacrylate, respectively. The resulting monomers were shown to have comparable or enhanced performance compared to styrene in diglycidyl ether of bisphenol A-based vinyl esters, for use in thermoset resins.

The second synthetic route to produce aromatic bio-based monomers from lignin is through a reaction with methacryloyl chloride (or acryloyl chloride). Abdelaty and Kuckling synthesized vanillin acrylate in 85% yield by reacting vanillin with acryloyl chloride.[525] A copolymer was then formed with NIPAAm through free radical polymerization, while post-polymerization modification were carried out by reacting the aldehyde on the vanillin moieties to form imines. Zhou and co-workers synthesized the acrylates and methacrylates of vanillin and syringaldehyde by reacting them with acryloyl chloride and methacryloyl chloride, respectively.[526] Yields of 65%, 60%, 63% and 50% were achieved for vanillin methacrylate, vanillin acrylate, syringaldehyde methacrylate and syringaldehyde acrylate, respectively. The resulting monomers were successfully used in a free radical polymerization with the syringaldehyde based polymers having a significantly greater $T_g$ (> 170 °C) than the vanillin-based (<110 °C) and petroleum-based polymers (<110 °C). In a final example, 4-propylsyringol and 4-propylguaiacol were reacted with acryloyl chloride to synthesize 4-propylsyringol acrylate and 4-propylguaiacol acrylate, respectively, with high purity and yields.[527] Controlled radical polymerization of these monomers was investigated and high molecular weights and low dispersity values (<1.44) were obtained. A low dispersity triblock, containing one of the bio-based monomers and *n*-butyl acrylate was also prepared, which showed promising thermal and mechanical properties.

Other aromatic platform chemicals, which are not derived from lignin, can be used to synthesis acrylate monomers. One example is piperonyl alcohol, which can be derived from piperine that is sourced from black pepper. There are several reported routes for the synthesis of piperonyl alcohol from piperine *via* the intermediate piperonal.[528] The first step to form the aldehyde intermediate involved either an oxidation with $KMnO_4$/THF or an ozonolysis with $O_3/H_2O$. The subsequent reduction to the alcohol product was carried out with either $NaBH_4$ or $Pt/H_2$. Once the alcohol was formed, the piperonyl methacrylate monomer was formed by a reaction with methacrylic anhydride, with a yield of 89% being obtained. The monomer was then investigated for potential use in water-based pressure sensitive adhesives. Cardanol is an aromatic lipid that is derived from cashew nutshell liquid. Cardanol contains a phenolic group that was reacted with acryloyl chloride at 40 °C for 8 h, to form cardanyl acrylates with differing R groups (Figure 38).[529] However, no yields were reported. Ladmiral and co-workers took a different approach to the synthesis of cardanol methacrylate, where the first step was the epoxidation of cardanol with epichlorohydrin and tetrabutylammonium chloride.[530] The epoxy product was obtained with a yield of 92% and was then subsequently reacted with methacrylic acid andtriphenylphosphine at 80 °C for 20 h. The product was formed with an 87% yield.

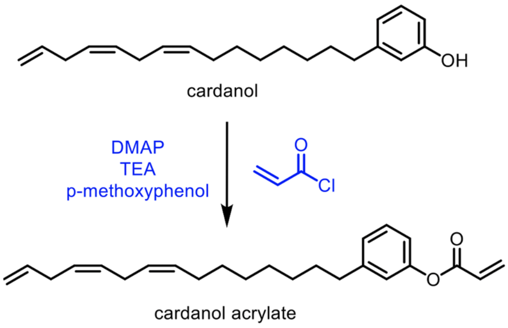


**Figure 38.** Synthesis of cardanol acrylate by coupling with acryloyl chloride.

The synthesis of acrylates and methacrylates has been vastly explored and a wide range of biomass has been used. Many of these routes offer large potential as alternative routes to synthesize important monomers without the use of crude oil. For commodity polymers, such as acrylic acid and methacrylic

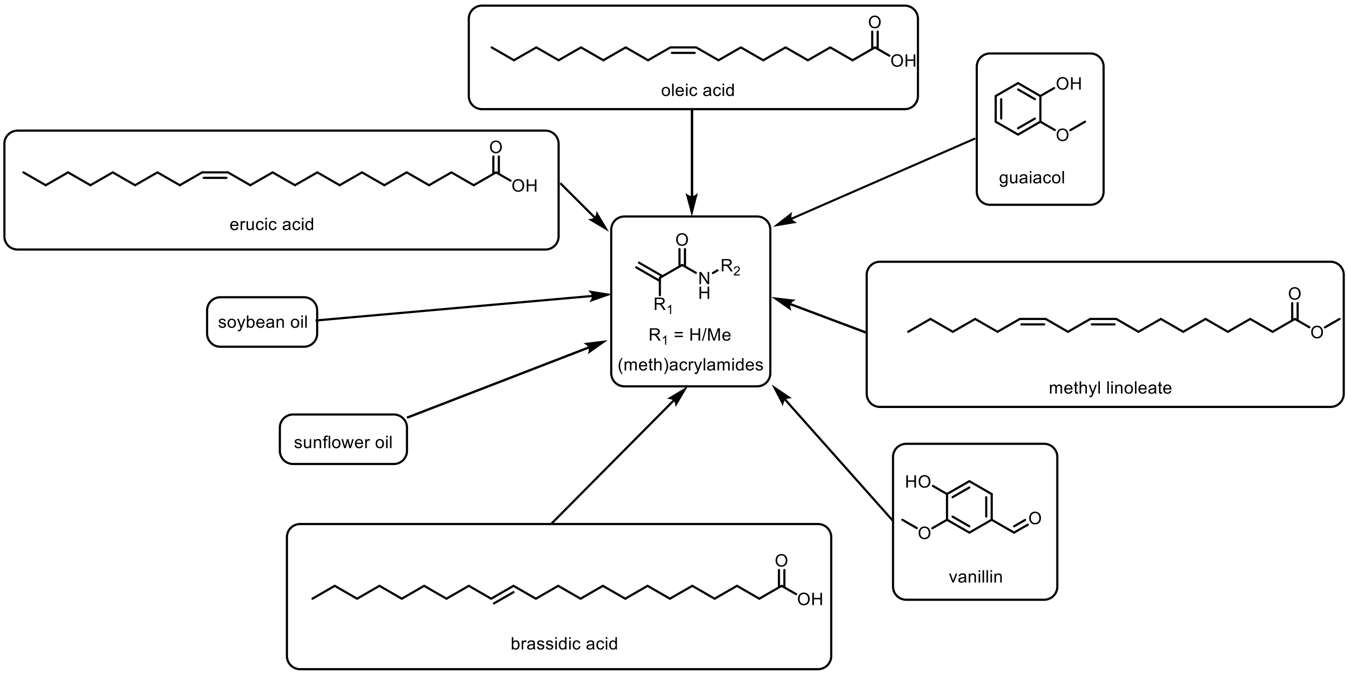


**Figure 39.** Structures of the different bio-based feedstock for the production of (meth)acrylamides.

acid, there are several different feedstocks that can be used and all offer advantages and disadvantages, for example, glycerol is a by-product from biodiesel production and is, therefore, readily available. However, when crude glycerol was used lower yields were obtained and thus, expensive purification methods were required prior to the monomer synthesis being carried out.[173,259] For many of the processes that have been developed to synthesize acrylic acid and methacrylic acid from biomass, complex catalysts and high operating temperatures are required and this significantly limits the sustainability of these processes. Furthermore, many of these processes are plagued by low yields, with the most significant example being the synthesis of methacrylic acid from isobutane, when low conversions resulted in yields <10%.

Further to the synthesis of commonly used acrylic monomers, more complex monomer structures have been synthesized by using the unique structures of natural compounds. These include monomers synthesized from vegetable oils, terpenes, isosorbide and lignin. In contrast to the procedures for acrylic acid and methacrylic acid, low temperatures are used in these procedures. However, these methods consist of long multi-step organic syntheses, thus hindering yields, and often involves the use of toxic reagents. Due to the feedstock used, the structures of these monomers differ significantly from commonly used conventional monomers and, therefore, they do not act as direct replacements. However, the complex structures of these monomers offer unique properties, for example, the terpene and isosorbide derived monomers offer improved rigidity, due to their cyclic structures. While these developments in the synthesis of these monomers from biomass offers a great deal of potential, problems with high temperatures, the use of complex catalysts and poor yields and selectivity must be overcome for these methods to become viable to replace the petrochemical monomer synthesis.

### 3.2. (Meth)acrylamides

Acrylamide is a toxic water-soluble monomer that is derived from the hydration of acrylonitrile. While poly(acrylamide)s have many applications, including as flocculants, poly(*N*-isopropylacrylamide) (PNIPAAm) is one of the most widely studied and is well known for its thermoresponsive behavior. Indeed, hydrogels based on PNIPAAm are used in many fields including astronomy, energy and in the biomedical field, especially in drug delivery and tissue engineering. Like for acrylic monomers, acrylamide monomers can be produced from biomass. However, examples of bio-based acrylamides have been much less reported and only a handful of synthetic procedures have been highlighted. Whereas when considering (meth)acrylates, the most used monomers (acrylic acid, methacrylic acid, methyl acrylate and methyl methacrylate) have had their potential synthetic routes from biomass investigated, there has been very little research into the synthesis of acrylamide or NIPAAm from biomass. Thus, in this section, the focus is on those examples of forming bio-based acrylamides from vegetable oils, either through the functionalization of carbon−carbon double bonds or the acid functionality, and the lignin derived guaiacol and vanillin. The structures of the resulting monomers are very different from the most commonly used acrylamides and so do not act as a direct replacement for conventionally derived acrylamides. The structures of some of the bio-based feedstock to produce (meth)acrylamides are displayed in Figure 39. Similar to their acrylate counterparts, (meth)acrylamide processes are not entirely bio-based as coupling agents such as acryloyl chloride are used.

Acrylamidation of fatty acids and fatty esters have been reported as one synthetic method to form bio-based acrylamides.[388] As with the production of acrylates from vegetable oils, either the carbon−carbon double bonds or the carboxylic group can be functionalized.[388] When considering reacting the alkene bond, the double bond was protonated with concentrated sulfuric acid, forming a carbocation.[388,531]

The carbocation can then react with a nucleophilic nitrile, which forms an amine upon hydrolysis. Some examples of acrylamides derived *via* this method are displayed in Figure 40.

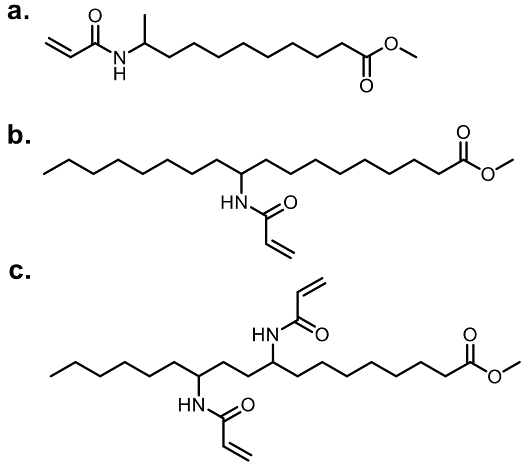


**Figure 40.** Examples of acrylamides derived from methyl 10-undecanoate (a), methyl oleate (b) and methyl linoleate (c).

The first example of this applied to fatty acids was reported by Roe and Swern in 1953 where the addition of different nitriles to oleic acid was investigated.[532] When acrylonitrile was used, an acrylamide was formed with 89% yield. Sinnreich *et al.* investigated the same reaction for a wider range of fatty acids including erucic acid and brassidinic acid.[533] Eren and co-workers synthesized several acrylamides including methyl oleate acrylamide, methyl linoleate acrylamide, sunflower oil acrylamide and soybean oil acrylamide.[534] The yields reported for the linoleate acrylamide, sunflower oil acrylamide and soybean oil acrylamide were 60%, 50% and 45%, respectively.

Acrylamides can also be formed through acrylamidation of the carboxylic functionality of fatty acids, with an example illustrated in Figure 41. Tarnavchyk *et al.* reported a transesterification of triglycerides from soybean oil with *N*-(hydroxyethyl)acrylamide in the presence of sodium hydroxide at room temperature.[535] The resulting acrylamide monomer was formed in a 90% yield, and was subjected to free radical polymerization. Given the success in the monomer synthesis, it was expanded to include other oils, including sunflower oil, linseed oil and olive oil. Using THF as the solvent and sodium hydroxide as the catalyst allowed for yields of between 93% and 96% to be achieved.[536,537]

A final example of producing a bio-based acrylamide is a method using the lignin-derived chemicals guaiacol and vanillin, for which two approaches were devised.[22,538] The first approach was a single-step synthesis using guaiacol as the starting material (Figure 42a), and proceeded *via* a Friedel–Crafts alkylation with *N*-hydroxymethylacrylamide. However, low yields were reported for this synthetic route. When a strongly acidic cationic exchange resin was used as the catalyst, a yield of 25% was obtained after 4 days. When the catalyst was changed to sulfuric acid, the yield increased slightly to 31% with the same reaction time. It was shown that for both catalysts further increasing the reaction time did not lead to any improvement in the yield. The second approach was a three-step synthetic route starting with vanillin (Figure 42b). The first step was the formation of an oxime from vanillin through a reaction with hydroxylamine in the presence of hydrochloric acid, and a yield of 67% was reported. This was followed by a reduction with a Pd/C catalyst that proceeded to completion. The final step to form the acrylamide was a reaction with acryloyl chloride and a yield of 41% was obtained for the final step. The overall yield of the three-step synthesis was recorded as 27%.

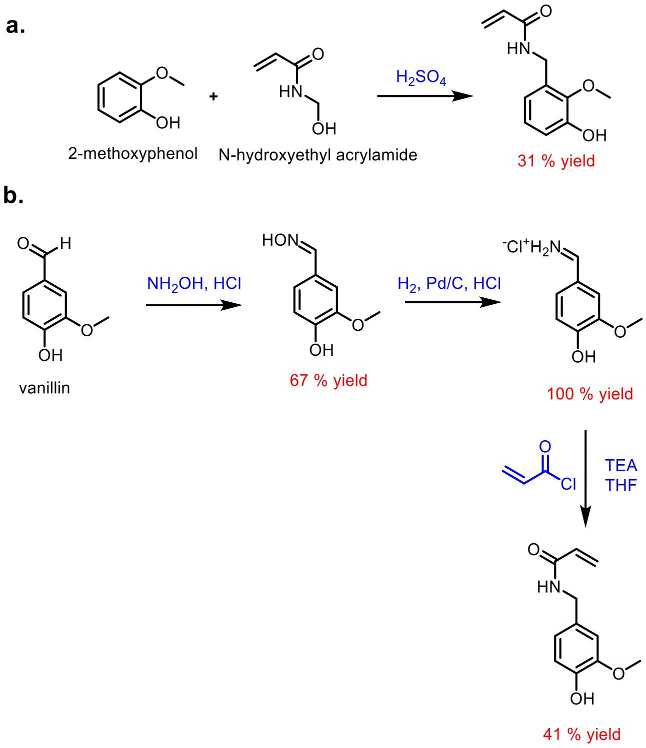


**Figure 42.** Two different routes to form aromatic acrylamide monomers *via* a single-step Friedel–Crafts reaction (a) or a multi-step reaction (b).

While the methods highlighted above show the potential to produce acrylamide monomers from biomass, the scope has thus far been very limited. The sources of biomass used in these methods results in monomers with structures that significantly differ from conventional used acrylamides, such as NIPAAm, and this hinders their potential applications on an industrial scale. Furthermore, several of the limited methods that have been investigated are plagued by low yields, require

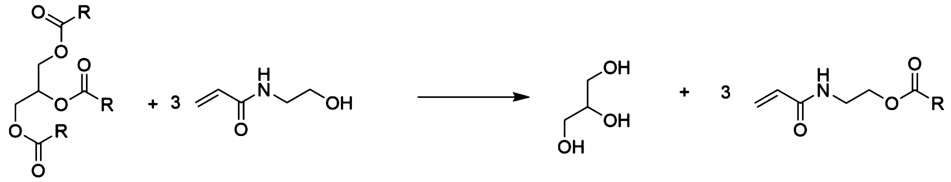


**Figure 41.** Transesterification of fatty esters to form acrylamide monomers.

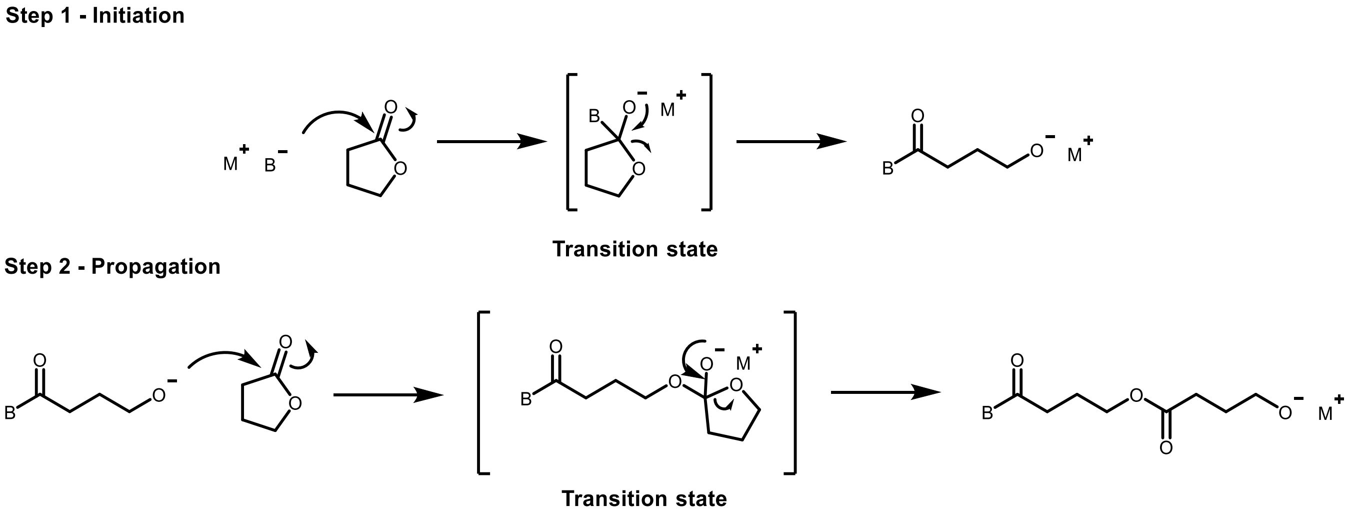


**Figure 43.** Mechanism for the ring-opening polymerization of lactones.

multiple steps or use hazardous reagents and catalysts. Therefore, improvements into these methods have to be explored, as well as the potential to increase the scope of biomass that can be used for the production of acrylamide monomers.

## 4. CYCLIC MONOMERS

### 4.1. Lactones

Lactones are cyclic esters that can be utilized to synthesize polyesters *via* ring-opening polymerization (ROP), of which the mechanism can be seen in Figure 43. The French chemist Théophile-Jules Pelouze first coined the term "lactone" when he derived the cyclic structure from lactic acid in 1844. Poly(lactone)s have the added benefit of possessing a regular repeating ester linkage along their backbone causing them to be biodegradable under mild conditions.

This review is designed to discuss monomers that are derivable from sustainable sources, and hence is not intended to offer a comprehensive review of all aspects of lactone polymer chemistry. Carlotti and co-workers provided an excellent review in 2020 highlighting the wide variety of lactones available and the range of potential initiators that can be employed.[539] Figure 44 shows the general lactone structures that are covered here and their sustainably sourced starting materials. First, ε-caprolactone is discussed, followed by δ-valerolactone, 5-membered rings, then propiolactone, and finally some other lactone structures are described.

**4.1.1. 7-Membered Lactones.** The emergence in recent years of tissue engineering within the field of biomaterials has sparked something of a renaissance in interest in poly(caprolactone)s. This is because poly(caprolactone)s exhibit superior viscoelastic and rheological properties compared to their counterparts, and possess the status of an FDA approved chemical.[540] Generally, the synthesis of ε-caprolactone is carried out by the Baeyer−Villiger oxidation of cyclohexanone; however, there are still opportunities to improve this well-developed synthetic route. For example, the oxidation step can be catalyzed by $SiO_2$ nanorods, which are reusable, easily separable and metal-free.[541] Furthermore, the oxidation can be carried out in ethyl acetate, which can be considered to be an environmentally friendly solvent. As well as chemical catalysis, biological-derived enzymes such as lipases have been shown to be extremely promising biocatalysts for the oxidation step, which remove the need for complex catalysts entirely.[542,543]

Increasingly, bioengineering has become a more important method for monomer synthesis in general, and the production of ε-caprolactone is no different. Bioengineering removes the need for metal catalysis and harmful solvents while relying on the enzymatic power of bacteria. One route to ε-caprolactone is *via* oxidation of cyclohexane by bacteria. Although cyclohexane is typically regarded as a petrochemical, it can be derived from sustainably sourced anisole with excellent selectivity.[544] Nonetheless, recent examples of the bioconversion of cyclohexane into ε-caprolactone tend to suffer from low conversion.[545] However, a recently bioengineered version of *Pseudomonas taiwanensis* was able to fully convert 5 mM cyclohexane into ε-caprolactone and 6-hydroxyhexanoic acid.[546]

Next to cyclohexane, 1,6-hexanediol can be considered as another sustainably sourced precursor for ε-caprolactone, as it can be derived from adipic acid and 5-hydroxymethylfurfural. 5-Hydroxymethylfurfural is a well-known renewable platform chemical, and adipic acid can be formed from the oxidation of fatty acids.[547] *Gluconobacter oxydans* has been shown to be able to oxidize 1,6-hexanediol into 6-hexanoic acid, which can then be chemically ring closed with a yield of around 73%.[548] Chemical catalysis can also be used to convert 1,6-hexanediol into ε-caprolactone. For example, Heeres et al. carefully optimized a four-step route to ε-caprolactone with an overall selectivity of 95%.[549] Silica supported copper is able to generate ε-caprolactone alongside 1-hexanol and 1,6-hexanediol,[550] and Pt-loaded $SnO_2$ can be used to lactonize 1,6-hexanediol with an 86% yield.[551]

Generally, the synthesis of ε-caprolactone is carried out by the Baeyer−Villiger oxidation of cyclohexanone, which in turn can be derived from bio-derived anisole *via* a hydrogenation and oxidation process (Figure 45).[552,553] However, there are still opportunities to improve this well-developed synthetic route.

Lastly, ε-caprolactone can even be derived from pinenes; however, the only example of this synthetic route requires four steps, making use of ozone, $AlCl_3$, a Ru catalyst, and mCPBA to give an overall moderate yield of 64%.[554]

**4.1.2. 6-Membered Lactones.** δ-Valerolactone is somewhat less recognized than ε-caprolactone; however, polymers

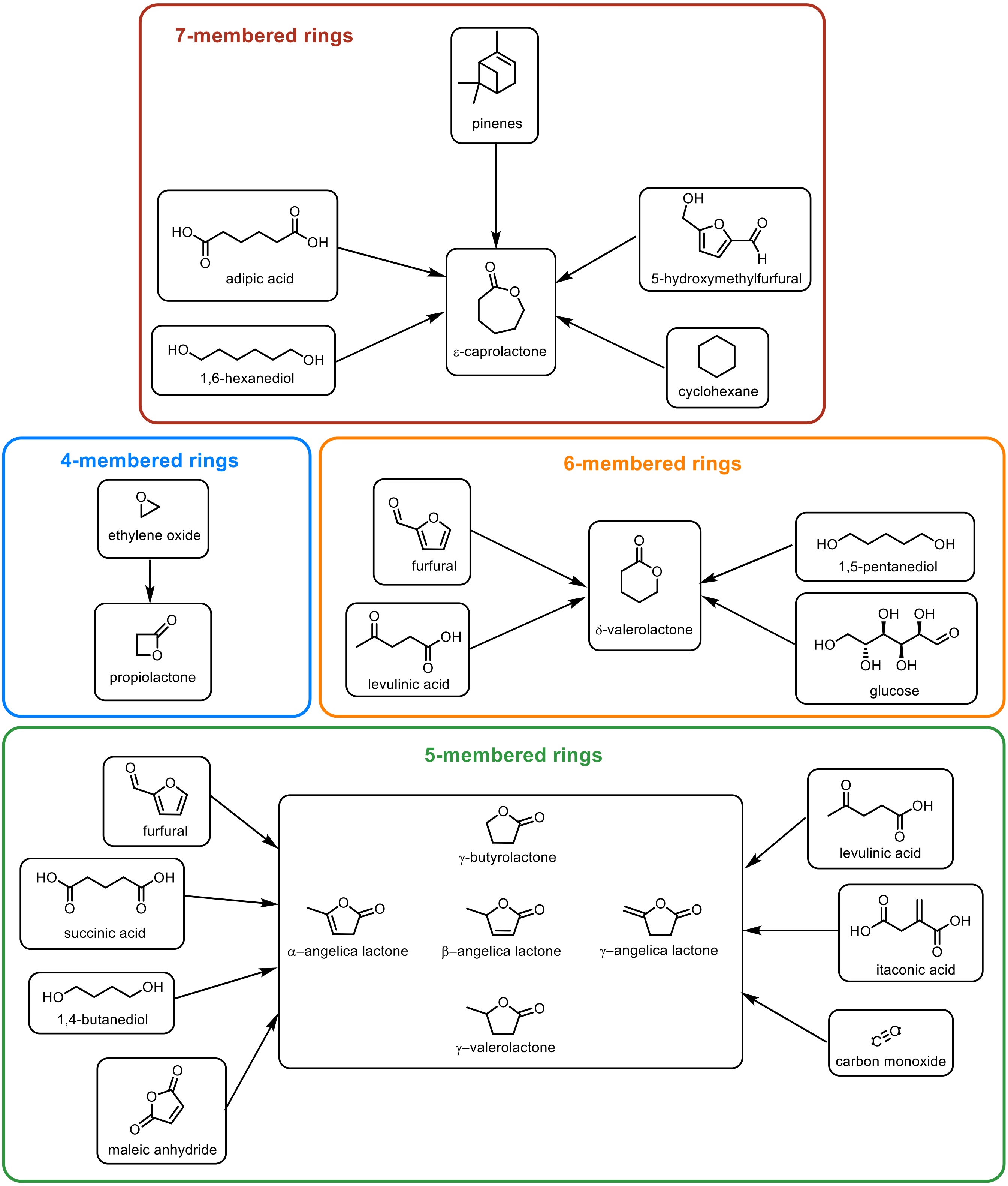


**Figure 44.** Sources of bio-based, sustainable lactone monomers.

synthesized from δ-valerolactone are versatile with good mechanical properties and degradability.[555] As was seen with ε-caprolactone, synthesis routes to δ-valerolactone from platform chemicals tend to require multiple steps and this is currently a disadvantage for the industrial viability of biomass-derived lactone monomers.

δ-Valerolactone can be made from a variety of platform chemicals and sustainably derived chemicals, including furfural, levulinic acid and 1,5-pentanediol. The routes discussed have positive and negative aspects, but they are all interesting and worth considering. Furfural is a well-known platform chemical,[13] and has been previously converted to δ-

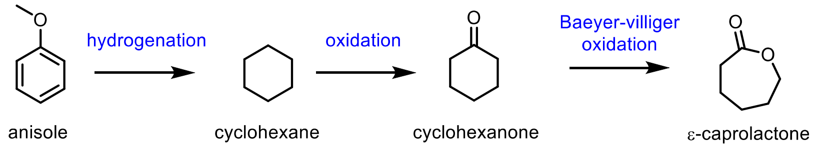


**Figure 45.** General scheme for the transformation of anisole to caprolactone.

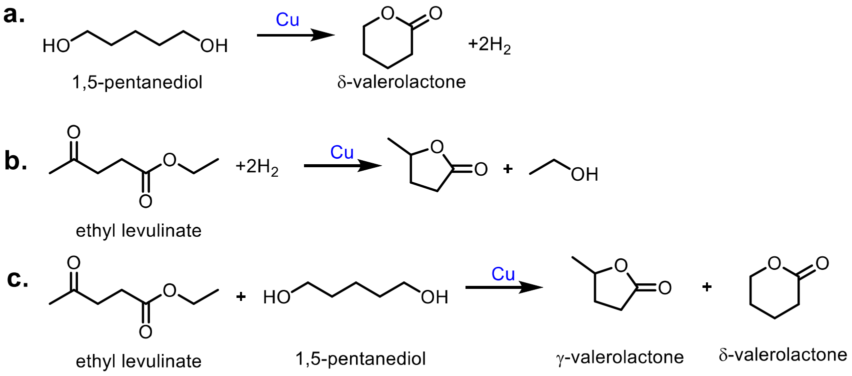


**Figure 46.** Synthesis protocols for valerolactones.

valerolactone by Tomishige and co-workers. They initially oxidized furfural to 2-furancarboxylic acid, which was then hydrogenated to form 5-hydroxyvaleric acid, followed by ring closure to δ-valerolactone. Unfortunately, the highest δ-valerolactone yield was only 7%; however, methyl 5-hydroxyvalerate was also produced with a 55% yield, which could subsequently ring closed to form δ-valerolactone. Furthermore, a platinum catalyst was required, diminishing the sustainability of the project. However, the catalyst could be regenerated by calcination.[556]

As an alternative to furfural, 1,5-pentanediol can also be used as a different sustainably sourced precursor for δ-valerolactone.[557] A route with mild conditions and high yields (> 98%) was achieved by coupling the dehydrogenation reaction of 1,5-pentanediol with the hydrogenation reaction of ethyl levulinate (Figure 46B).[558] This route also produces γ-valerolactone in high yield, but it is nonetheless an important route to sustainable 6-membered lactones. It should be noted that 1,5-pentanediol itself is not a platform chemical but can be derived from glutamic acid, which is an industrially scaled amino acid.

As well as furfural and 1,5-pentanediol, 6-membered lactones can be derived from levulinic acid. Levulinic acid is a promising platform chemical that can be synthesized on an industrial scale.[559] The procedure to make the lactone in question, 4-ketovalerolactone, required a bromination step in chloroform, followed by ring closure with triethylamine. Although this route is relatively straightforward requiring just two steps to the lactone, the use of halogenated solvents and bromine detract from the sustainable aspect of the work and benefit from improvements.[560]

An enzymatic approach can also be taken to produce δ-valerolactone, as opposed to a purely chemical synthesis. For example, isotactic, biodegradable poly(lactone)s have been made from β-methyl-δ-valerolactone, which in turn were prepared from glucose using enoate reductase enzymes.[561] Interestingly the isotactic polymers were amorphous like their atactic counterpart, and also had a similar softening temperature (221 K). The main benefit of taking an enzymatic approach is that they are generally much more specific than a chemical catalyst.

Although many of the routes here use well-known platform chemicals, they require several steps and often chemicals that are of environmental concerns.

### 4.1.3. 5-Membered Lactones.

There are several different bio-based 5-membered lactones including γ-butyrolactone, isomers of angelica lactone and γ-valerolactone. There is a plethora of sustainable routes to 5-membered lactones, which is due to the large number of potential precursors including succinic acid, fumaric acid, and maleic anhydride. In this section, first γ-butyrolactone is discussed as it is the most simple 5-membered lactone, followed by γ-valerolactone and then the angelica lactones, before any anomalous lactones are discussed.

#### *4.1.3.1. γ-Butyrolactone.*

γ-Butyrolactone is of interest to the sustainable chemist because of the diverse range of bio-based feedstocks that it can be derived from. In fact, of all the lactone and lactam rings explored in this review, γ-butyrolactone has the widest range of potential bio-based starting materials. Nonetheless, γ-butyrolactones do have one major issue, which is the difficulty in polymerizing them *via* ring-opening polymerization. This is because γ-butyrolactone is a 5-membered ring and possesses relatively low ring strain, which does not bring about a sufficient change in enthalpy upon its ring-opening to offset the entropic cost of polymer formation. Moreover, extreme conditions such as 20 000 atm and 160 °C were shown to only be sufficient to produce oligomers.[28] More recently, new techniques such as copolymerization with other lactones, and the use of powerful initiators (e.g. BuLi) has allowed the polymerization of γ-butyrolactone to yield polymers with molecular weights of over 10 kDa that are degradable.[562,563]

One of the more common feedstocks for γ-butyrolactone is succinic acid, which is another well-known platform chemical.[564] The conversion of succinic acid to γ-butyrolactone requires a catalyst, which has been the focus of numerous investigations. Here, some of the more recently developed catalytic systems (post-2010) to obtain γ-butyrolactone from succinic acid are highlighted. An overview of these catalysts, conditions, selectivity, and γ-butyrolactone yield is presented in Table 12. The generally taken approach for the production of

Table 12. Different Catalytic Systems for the Formation of γ-Butyrolactone from Succinic Acid

| Catalyst | Solvent | Temperature (°C) | Pressure (bar) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| Pd/$Al_2O_3$ | 1,4-Dioxane | 260 | 60 | 64 | 70 | 45 | 567 |
| Pd/$Al_2O_3$ | 1,4-Dioxane | 240 | 60 | 81 | 69 | 56 | 568 |
| Pd/$Al_2O_3$ | 1,4-Dioxane | 240 | 60 | 79 | 65 | 51 | 569 |
| Pd/$Al_2O_3$ | 1,4-Dioxane | 240 | 60 | 97 | 94 | 91 | 570 |
| Pd/$SiO_2$ | EtOH + water | 250 | 100 | 65 | 39 | 25 | 571 |
| Pd/$TiO_2$ | Water | 160 | 150 | 75 | 95 | 71 | 572 |
| Pd-Re/$TiO_2$ | Water | 160 | 150 | > 50 | 95 | 48 | 573 |
| Pd-Re/$TiO_2$ | 1,4-Dioxane | 140 | 80 | > 99 | 56 | 56 | 574 |
| Pd-Re/C | Water | 240 | 80 | 92 | nr | 67 | 575 |
| Pd-Cu/$Al_2O_3$ | 2-Isopropanol | 190 | 70 | 72 | 94 | 68 | 576 |
| Ru(acac)$_3$-triphos[a] | Methanol | 120 | 80 | 96 | nr | 76 | 577 |
| Ru/$SiO_2$ | 1,4-Dioxane | 200 | 50 | nr | nr | 90 | 578 |
| Ru/C | 1,4-Dioxane | 240 | 60 | 90 | 74 | 67 | 579 |
| Ru/C | 1,4-Dioxane | 240 | 80 | 45 | 98 | 44 | 580 |
| Ru/C | 1,4-Dioxane | 240 | 80 | 95 | nr | 20 | 581 |
| Re-Cu/C | 1,4-Dioxane | 240 | 80 | 100 | 23 | 23 | 582 |
| Re-Ru/C | 1,4-Dioxane | 140 | 80 | 64 | 75 | 48 | 583 |
| Re/C | Water | 240 | 80 | 34 | 93 | 32 | 584 |
| Re/C | 1,4-Dioxane | 240 | 80 | 80 | 77 | 62 | 585 |
| Mo/$TiO_2$ | Water | 240 | 150 | 81 | 68 | 55 | 586 |
| Ir/C | Water | 240 | 150 | 72 | 88 | 63 | 587 |

[a] Triphos: 1,1,1-tris(diphenylphosphinomethyl)ethane.

Table 13. Catalysts, Conditions and Yields for γ-Butyrolactone from Furfural/Furanone

| Catalyst | Solvent | Temperature (°C) | Pressure (bar) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| Pd/$SiO_2$ | Methanol | 80 | 35 | 100 | 77 | 77 | 592 |
| Ni-Fe/$SiO_2$ | Methanol | 80 | 35 | 100 | 90 | 90 | 593 |
| Pt-Ni/$SiO_2$ | Methanol | 80 | 3.5 | 100 | 78 | 78 | 594 |
| Pt-Ni/$SiO_2$ | Methanol | 80 | 35 | 100 | 76 | 76 | 595 |
| Pt/$Al_2O_3$ | Methanol | 80 | 35 | 100 | 61 | 61 | 595 |
| Pt-Ni/$ZrO_2$ | Methanol | 80 | 35 | 100 | 51 | 51 | 595 |
| Pt-Ni/$TiO_2$ | Methanol | 80 | 35 | 100 | 59 | 59 | 595 |
| Pt-Ni/$TiO_2$-$ZrO_2$ | Methanol | 80 | 35 | 100 | 55 | 55 | 595 |
| Pt-$Nb_5Zr_5$/solid acid | 1,4-Dioxane | 140 | 50 | 100 | 97 | 97 | 596 |

γ-butyrolactone from succinic acid is liquid phase hydrogenation. The best catalysts typically use Pd/Pt/Ru metals as they are the most efficient. Moreover, the catalytic metal is generally supported on a framework and significant efforts have been undertaken to improve the catalytic performance of these supported metals.

The main problem with using succinic acid as a feedstock for γ-butyrolactone production is that of catalyst selectivity. Succinic acid can be transformed into other chemicals such as 1,4-butanediol, maleic anhydride, and succinic anhydride amongst others, and therefore reaction optimization is important.[565] Hence, many of the reactions use high temperatures and high pressures, as well as less environmentally preferred solvents, all of which are disadvantageous in terms of the overall sustainability of γ-butyrolactone production.

Another well-known bio-based acid is fumaric acid, which can be hydrogenated to succinic acid and then subsequently converted into γ-butyrolactone; however, this is much less reported than the direct conversion of succinic acid. This has been performed recently with the use of a silica supported Pd−Re catalyst with a selectivity of 91% toward γ-butyrolactone, supported by the use of computer modelling.[566]

Furfural is a platform chemical that is derived from the hydrolysis and subsequent dehydration of xylan, which is a polysaccharide found in lignocellulosic biomass.[588] In more recent times, the conversion of furfural into other useful chemicals, including γ-butyrolactone has begun to be explored.[589,590] Generally, the first step to γ-butyrolactone from furfural is the conversion of furfural into furanone; however, other furfural derivatives can be used to make γ-butyrolactone. For example, a metal-free route to γ-butyrolactone was presented very recently, whereby derivatives of furfural such as tetrahydrofurfuryl alcohol were aerobically oxidized with mesoporous carbon nitride as a catalyst to yield γ-butyrolactone.[591] Using this method, tetrahydrofurfuric acid was able to be converted into γ-butyrolactone with a yield of around 85%, under very mild conditions. The conversion of furanone to γ-butyrolactone requires catalysis, and several examples have been reported in the literature (see Table 13). As with succinic acid, the catalysts are required for hydrogenation, and Pt and Pd are typically the best metals for this. The examples below typically focus on mixing the metal catalyst with dopants, and how they are fixed to the solid support.

1,4-butanediol can be derived from natural sugars such as dextrose, making this an important chemical for sustainably

https://doi.org/10.1021/acs.chemrev.2c00354

**Table 14. Catalysts, Conditions and Yields for γ-Butyrolactone from 1,4-Butanediol**

| Catalyst | Solvent | Temperature (°C) | Pressure (bar) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| $Cu/SiO_2$ | No solvent | 250 | 1 | >99 | >99 | >99 | 601 |
| $Cu/SiO_2$ | No solvent | 250 | 1 | nr | nr | 97 | 602 |
| $Cu/Al_2O_3$ | 1,4-Dioxane | 250 | 16 | 100 | 98 | 98 | 603 |
| Cu(Co,Cr,Zn)/MgO | No solvent | 250 | 1 | 95 | 96 | 91 | 598 |
| $Cu/La_2O_3$-$ZrO_2$ | No solvent | 250 | 1 | 97 | 96 | 93 | 604 |
| $Cu/CeO_2$ | No solvent | 250 | 1 | 93 | 98 | 91 | 605 |
| $Cu/SiO_2$ | No solvent | 250 | 1 | 100 | 98 | 98 | 606 |
| $Cu/CeO_2$-$Al_2O_3$ | No solvent | 240 | 1 | 100 | 99 | 99 | 607 |
| Cu/MgO | No solvent | 250 | 1 | 70 | 99 | 69 | 599 |
| $Cu_2/Zn_2Mg_2Al_2O_7$ | No solvent | 240 | 1 | 71 | >99 | 70 | 608 |
| $Au/FeO_x$ | TBP | 140 | 12.5 | 100 | 86 | 86 | 609 |
| Au-Fe/$Al_2O_3$ | TBP | 140 | 12.5 | 100 | 88 | 88 | 610 |
| $Au/Mn_2O_3$ | TBP | 120 | 12.5 | 98 | 98 | 96 | 611 |
| Co-Cu/MgO | No solvent | 250 | 1 | 95 | 98 | 96 | 612 |
| Ir/bipy | 1,2-DME | 84 | 1 | nr | nr | 100 | 600 |

**Table 15. Catalysts, Conditions and Yields for Γ-Butyrolactone from Maleic Anhydride; $sCO_2$, Supercritical Carbon Dioxide**

| Catalyst | Solvent | Temperature (°C) | Pressure (bar) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| $Pd/Al_2O_3$ | $scCO_2$ | 200 | 120 | 100 | 80 | 80 | 613 |
| $Pd/Al_2O_3$ | $scCO_2$ | 200 | 120 $CO_2$, 21 $H_2$ | 100 | 80 | 80 | 614 |
| Pd/C | $scCO_2$ | 200 | 140 | 100 | 93 | 93 | 615 |
| Cu-$CeO_2/Al_2O_3$ | No solvent | 220 | 1 | 100 | 100 | 100 | 616 |
| Cu-$CeO_2/Al_2O_3$ | No solvent | 240 | 1 | 100 | 100 | 100 | 617 |
| Cu-ZnO/$SiO_2$ | No solvent | 220 | 1 | ~96 | ~96 | ~92 | 618 |
| Cu-Ni/$Al_2O_3$-$SiO_2$ | No solvent | 220 | 1 | nr | 90 | 85 | 619 |
| $Ni/Al_2O_3$-$SiO_2$ | No solvent | 220 | 1 | nr | 89 | 83 | 620 |

**Table 16. Catalysts, Conditions and Yields for γ-Valerolactone from Levulinic Acid; CNT, Carbon Nanotube**

| Catalyst | Solvent | Temperature (°C) | Pressure (bar) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| Co-Re/$TiO_2$ | 1,4-Dioxane | 220 | nr | >99 | >99 | >99 | 622 |
| Co/C | Water | 220 | 20 | 100 | 100 | 100 | 623 |
| Co[a] | Water | 150 | 30 | 99 | 92 | 91 | 624 |
| $Co/SiO_2$ | No solvent | 200 | 30 | 100 | 98 | 98 | 625 |
| Ni/C | 2-Isopropanol | 200 | n/a | >99 | >99 | >99 | 626 |
| $Ni(OAc)_2$ | No solvent | 200 | n/a | n/a | n/a | 98 | 627 |
| Ni-Pd/$Al_2O_3$ | Water | 190 | n/a | 83 | 79 | 66 | 628 |
| Zr-Al/β-zeolite | 2-Isopropanol | 170 | n/a | 95 | n/a | 90 | 629 |
| $ZrO_2$[b] | Ethanol | 250 | n/a | 100 | ~70 | ~70 | 630 |
| Ru/CNT | Water | 120 | 30 ($H_2$) | 86 | > 99 | 85 | 631 |
| $Ru/RuO_2 \cdot xH_2O$ | Water | 100 | 10 ($H_2$) | 100 | 100 | 100 | 632 |
| Ru/MIL-101-$S_{100}$ | Water | 80 | 5 | 99 | 87 | 86 | 633 |
| $CePO_4$ | 2-Isopropanol | 140 | n/a | 97 | 78 | 76 | 634 |
| $CePO_4/Co_2P$ | Water | 90 | 40 | 98 | 97 | 95 | 635 |
| $Pt/ZrO_2$ | Water | 240 | n/a | 97 | n/a | 90 | 636 |
| Hf/zeolite | 2-Isopropanol | 120 | 10 | 95 | 93 | 88 | 637 |
| Cu-Ni/$SiO_2$[c] | 2-Isopropanol | 120 | 40 | 99 | 97 | 96 | 638 |

[a] Prepared in ethanol. [b] High surface area. [c] Nanosphere. MIL-101-$S_{100}$ is a metal organic framework.

derived chemicals.[597] Furthermore, the transformation of 1,4 butanediol into γ-butyrolactone produces minimal waste with the only side product being 2 equiv of hydrogen. In fact, the dehydrogenation of 1,4-butanediol can be used *in situ* to act as a hydrogen source for hydrogenation reactions.[598,599] Interestingly, the reversible nature of the hydrogenation/dehydrogenation reactions between 1,4-butanediol and γ-butyrolactone result in a potential hydrogen storage system.[600]

Table 14 shows some of the more recent examples of the transformation of 1,4-butanediol into γ-butyrolactone. All examples use metal catalysis, which is not desirable; however, the conversion of 1,4-butanediol is generally very high, as well as the selectivity toward γ-butyrolactone. In general, the transformations are carried out in the vapor phase at elevated temperature, which result in an energy intensive process. However, readily available and safe metals such as copper can be used for catalysis. Nonetheless, one of the main disadvantages to these catalysts is their reduction in activity over time. Dopants such as $La_2O_3$ and $Cr_2O_3$ can be used to reduce catalyst poisoning further increasing the lifespan of the metals.

The hydrogenation of maleic anhydride is an important process for the production of several chemicals including γ-butyrolactone, tetrahydrofuran and succinic anhydride. In Table 15, several catalysts can be seen with their associated conditions. Many of these catalysts lose potency after several hours of reaction, so the yield of butyrolactone mentioned is the maximum yield at any point of reaction. There are two main methods for the production of γ-butyrolactone derived from maleic anhydride. First, the use of supercritical $CO_2$ ($sCO_2$) as a solvent, which is environmentally friendly and is excellent at dissolving reactive gases such as hydrogen and oxygen; however, they require expensive palladium-based catalysis. The alternative method uses gas phase hydrogenation of maleic anhydride, which requires lower pressures and employs the use of cheaper metal catalysts such as copper. The Cu-$CeO_2$ catalysts employed are very promising showing 100% conversion of maleic anhydride with complete selectivity toward γ-butyrolactone.

Finally, carbon monoxide can be used to make γ-butyrolactone *via* cyclotetramerization with a trinuclear titanium polyhydride complex.[621] This method was able to yield γ-butyrolactone in 55% yield, with the by-product being methanol, thus showing a promising technology that can convert carbon monoxide into compounds useful for polymerization.

*4.1.3.2. γ-Valerolactone.* As mentioned earlier, levulinic acid is a promising platform chemical that can be transformed into various other fine chemicals. In fact, levulinic acid is the most common precursor for γ-valerolactone production. This is because the transformation of levulinic acid into γ-valerolactone follows a simple cascade type reaction where it is initially hydrogenated and then subsequently cyclized to form γ-valerolactone. Generally, catalysts are heterogenous with molecular hydrogen used as a hydrogen source as this is generally the most efficient route that is suitable for industry. For a sustainable process, water is a good solvent from a sustainablity point of view; however, once levulinic acid is dissolved, it becomes acidic and catalyst leaching can occur, thus other solvents are frequently used. In Table 16, various examples of different catalysts and conditions can be seen, with their associated yield of γ-valerolactone. Given the numerous examples of different catalysts that have been reported, only literature examples post-2018 have been selected.

Furfural can be converted into γ-valerolactone using a variety of different methods. Although not as well developed as the transformation of levulinic acid into γ-valerolactone, moderate yields (i.e., 65−86%) of γ-valerolactone from furfural are obtainable. The production of γ-valerolactone from furfural requires several steps.[639] First, a transfer hydrogenation step is carried out with the use of a Lewis acid to convert the furfural into furfural alcohol/ether. Next, a Lewis acid is used to ring open the furfural alcohol/ether to a levulinate ester. The levulinate ester then undergoes a subsequent transfer hydrogenation to form 4-hydroxypentanoate, which can then be lactonized (Figure 47).

The transfer hydrogenation step is also known as a Meerwein−Ponndorf−Verley (MPV) reaction and has the benefit of avoiding the use of gaseous hydrogen. Solvents such as 2-isopropanol are typically used as they act as a proton source for hydrogenation. Popular catalysts tend to center around the use of a combination of Lewis acid metal sites embedded in alumina/silica zeolites as they are highly selective.

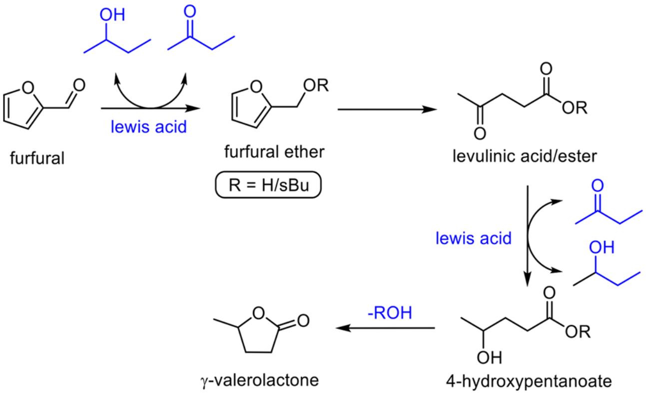


**Figure 47.** Preparation of γ-valerolactone starting from furfural.

Table 17 highlights the most recent catalytic systems for the transformation of furfural into γ-valerolactone. Generally, Lewis acid sites in zeolites in combination with alcohols are used as a hydrogen source. One notable example is the use of organophosphate polymers prepared from vinylphosphonic acid, *p*-toluenesulfonic acid and $HfCl_4$. These polymers were very effective catalysts that showed excellent recyclability, demonstrating the power of polymers as a framework for catalysts.

*4.1.3.3. Angelica Lactones.* The majority of angelica lactone is produced as an intermediate or a by-product during the synthesis of γ-valerolactone, and thus the literature on angelica lactones is rather underdeveloped. However, there are examples of its use in polymer chemistry.[646,647] Furthermore, angelica lactone contains a double bond, which could enable its radical polymerization and thereby broaden the scope of this lactone in the field of polymer chemistry.

Catalysts in the literature generally upscale platform chemicals such as levulinic acid into a range of fine chemicals including angelica lactones. However, there are examples where the synthesis of angelica lactone is targeted and thus are especially high yielding. For instance, $SiO_2$ is reported to be the most efficient catalysts for the formation of angelica from levulinic acid, and this was demonstrated by Sato and co-workers when they managed an angelica lactone yield of 86% with a levulinic acid conversion of 95%.[648] Generally, the selectivity toward α- and β-angelica lactones was around 30−40%, while γ-angelica lactone was obtained in 5% conversion. It must be noted that the reaction required decreased pressure and a temperature of around 550 K to generate this yield, highlighting how energy intensive the synthesis process is. Another example used a HZSM5/$SiO_2$ catalyst to generate an angelica lactone yield of 97% consisting of 64% α-angelica lactone and 33% of the β-angelica derivative.[649] This route was less energy intensive as it required a lower temperature of 403 K and a pressure of 0.1 bar. Montmorillonite K10 clay has been shown to be able to convert levulinic acid to angelica lactone with a yield of 92% at a temperature 438 K and pressure of 0.067 bar.[650] Finally, $WO_3$/Al-HZSM-5 catalysts can convert levulinic acid into angelica lactone and ethyl levulinate. The catalyst managed to obtain levulinic acid conversions of up to 98% with a selectivity toward angelica lactone of 75%.[651] Many other catalysts that have been screened do not target angelica lactone in specific, and thus the corresponding yields of angelica lactone are lower, for example, the use of a Sn/Al zeolite beta catalyst to upscale furfural. The best performing catalyst system managed to convert 95% of the

Table 17. Catalysts, Conditions and Yields for γ-Valerolactone from Furfural

| Catalyst | Solvent | Temperature (C) | Pressure (bar) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| Organophosphate-Hf/polymers | 2-Isopropanol | 180 | n/a | 100 | 81 | 81 | 640 |
| Hf/USY zeolite | 2-Isopropanol | 140 | n/a | 100 | 65 | 65 | 641 |
| Mesoporous $HSO_3/Al_2O_3$ | 2-Butanol | 120 | n/a | 100 | 86 | 86 | 642 |
| Zr-TPA/$SiO_2$[a] | 2-Isopropanol | 170 | n/a | 100 | 81 | 81 | 643 |
| $ZrPO_4$/SAPO-34[b] | 2-Isopropanol | 150 | n/a | 100 | 80 | 80 | 644 |
| AuRu/$ZrO_2$ | 2-Isopropanol | 150 | 5 ($N_2$) | ~85 | 80 | 68 | 645 |

[a]TPA: terephthalic acid. [b]SAPO-34: silicoaluminophosphate zeolite.

inputted furfural after 24 h, with the main products being furfuryl 2-butyl ether, levulinic acid, and angelica lactones with a selectivity of 29%, 14% and 23%, respectively.[652]

Itaconic acid can be used as a bio-based starting material for γ-angelica lactone. Itaconic acid is one of the top valued chemicals from biomass as described by the US Department of Energy, and can be used to form γ-angelica lactone (Figure 48).[485,653] First, itaconic acid monomethyl ester need to be partially reduced before it undergoes intramolecular cyclization to form γ-angelica lactone. This has been previously demonstrated to give a yield of 40−45%. The thus synthesized γ-angelica lactone was subsequently polymerized through the double bond to yield a polymer with pendant lactone groups, which could potentially then undergo ring-opening post-polymerization modification.

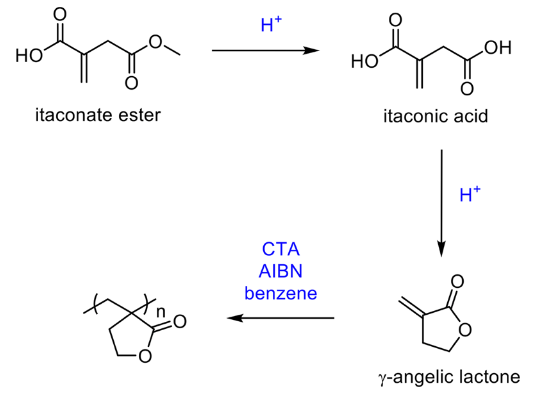


**Figure 48.** Synthesis of γ-angelica lactone from itaconic acid monomethyl ester, and its subsequent radical polymerization.

*4.1.3.4. Other 5-Membered Lactones.* 1,3-Dihydroxyacetone is a triose sugar that can be derived from biomass, which when combined with formic acid can be converted into α-hydroxy-γ-butyrolactone with the use of a Lewis acid catalyst, typically using tin as the metal center. Furthermore, these catalysts can also be used to convert other chemicals such as ethylene glycol and glycerol into lactones.[654]

**4.1.4. 4-Membered Lactones.** Much of the research into the synthesis of propiolactone is antiquated, of which many routes cannot be considered to be sustainable, with many procedures using multiple steps and harsh chemicals.[655,656] Of the very few methods to synthesis propiolactones, however, one route using ethylene oxide as a precursor material for the synthesis of β-propiolactone is a notable exception.[657] The latter relies on the carbonylation of ethylene oxide with carbon monoxide in the presence of a bimetallic aluminum/cobalt catalyst, resulting in >99% conversion of the ethylene oxide feed with a selectivity of over 96% toward β-propiolactone. Importantly, ethylene oxide can be derived from sustainable sources and thus this route is important for sustainable propiolactones (PLs).[658]

**4.1.5. Other Lactones.** Fatty acids can be used to make macrolactones, which can also be contracted to make 5- and 6-membered lactones with the use of a $W(OTf)_6$ catalyst.[659] Indeed, this method was able to produce γ-caprolactone from ε-caprolactone in 94% yield. Furthermore, the natural abundance of fatty acids makes this method an exciting prospect for further research.

Levoglucosenone is a 7-membered ring type structure that can be hydrogenated to form Cyrene, which is an emerging green, dipolar aprotic solvent that can replace less sustainable solvents such as DMF.[504] Furthermore, levoglucosenone and Cyrene can be oxidized with the use of aqueous hydrogen peroxide to form (S)-γ-hydroxymethyl-α,β-butenolide and (S)-γ-hydroxymethyl-γ-butyrolactone, respectively (Figure 49).

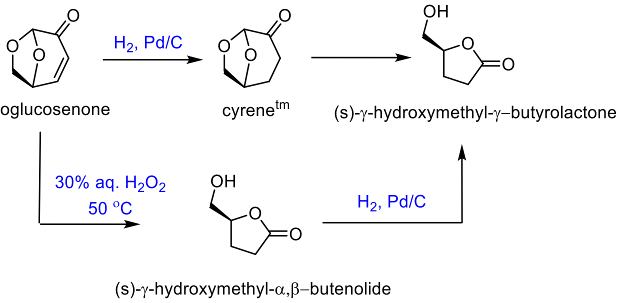


**Figure 49.** Formation of (S)-γ-hydroxymethyl-α,β-butenolide and (S)-γ-hydroxymethyl-γ-butyrolactone derived from levoglucosenone.

The conditions used were reasonably mild and the yields were generally above 80%, highlighting a facile route to sustainable lactones.[660] Furthermore, the (S)-γ-hydroxymethyl-α,β-butenolide could be converted into the lactone *via* hydrogenation.

As highlighted, multiple sustainable sources have been explored to produce various lactones that can serve as feedstock for ring-opened polymers. Some of the precursors used are more sustainable than others, and there is variety in the "greenness" of the transformations to lactones. A wide range of catalysts, solvents, temperatures, and pressures can be used with varying degrees of success. Furthermore, any polyester synthesized from the ring-opening polymerization of a lactone should theoretically be biodegradable due to the regular ester linkages that can be severed under acidic or basic conditions.

## 4.2. Lactams

Lactams are cyclic amides with an analogous structure to lactones, hence providing some overlapping opportunities as a chemical feedstock. For instance, the mechanism for the ring-opening polymerization of lactams is essentially the same as

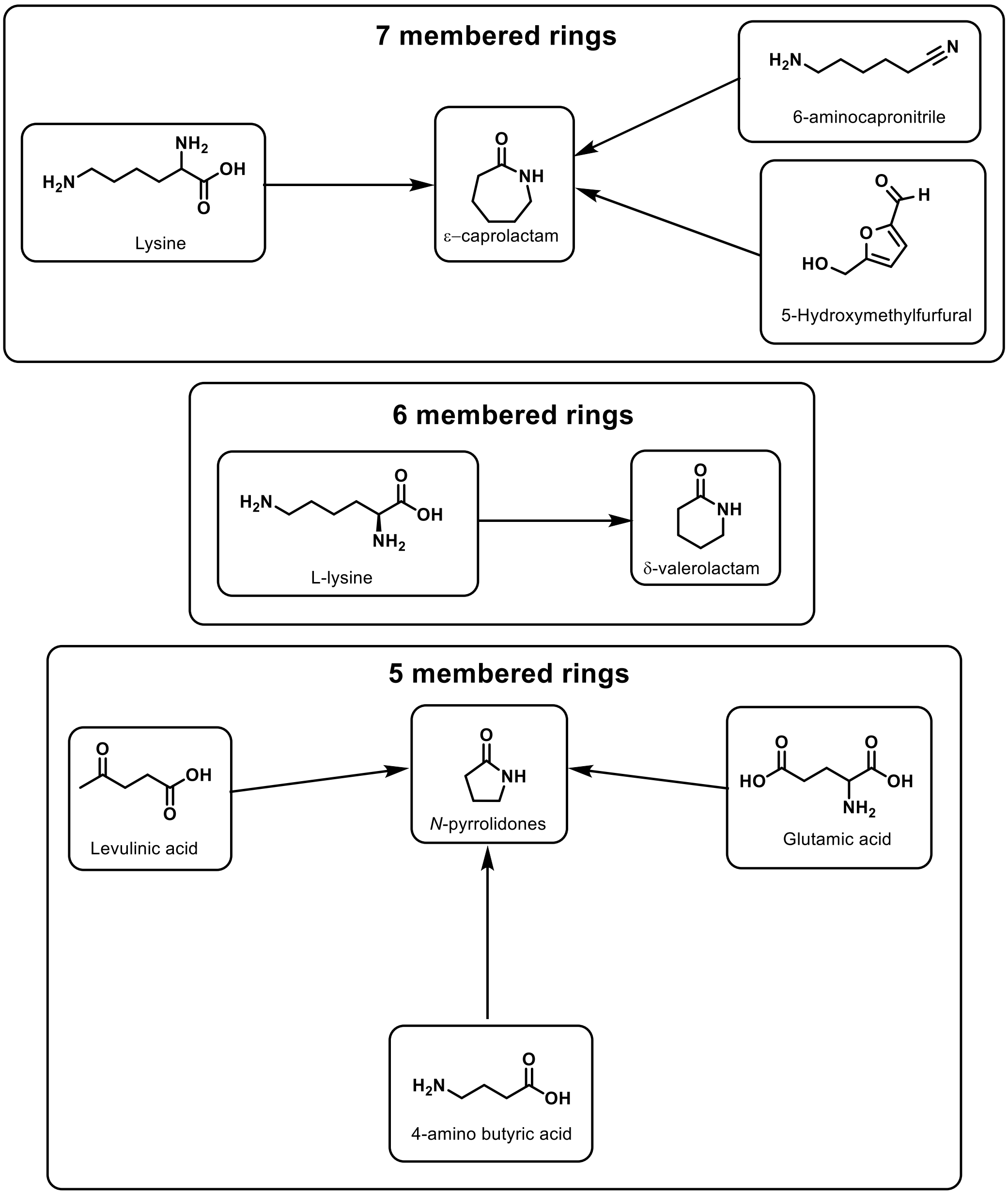


**Figure 50.** Sources of bio-based, sustainable lactams.

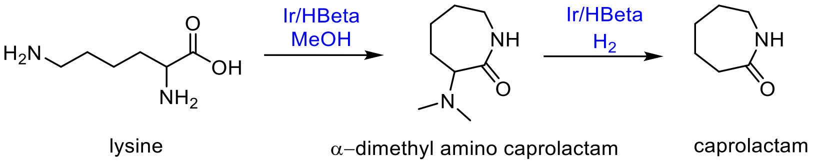


**Figure 51.** Ring closure of lysine to $\alpha$-dimethyl amino caprolactam followed by amine removal with Ir catalyst.

that of lactones, except that a polyamide is formed instead of a polyester. Amide bonds are more difficult to degrade in comparison to esters and this results in more durable and resistant polymers. In this section, the synthesis of $\varepsilon$-caprolactam from sustainable feedstocks is discussed, followed by $\delta$-valerolactam, then *N*-pyrrolidones (Figure 50).

**4.2.1. 7-Membered Lactams.** $\varepsilon$-Caprolactam is one of the most important plastic commodity chemicals in the world as the ring-opening polymerization of $\varepsilon$-caprolactam produces Nylon-6. Nylon-6 is very tough and extremely durable, thus difficult to degrade, and so finds applications as weather-resistant fibers and materials.[661] $\varepsilon$-Caprolactam is generally made on an industrial scale *via* the Beckmann rearrangement of cyclohexanone; however, there are several major environmental disadvantages to this route. First, cyclohexanone is produced from the aerobic oxidation of cyclohexane, but the conversion must be kept extremely low (i.e., 3−6%) to maintain high selectivity. Second, the major by-product of the conversion of cyclohexanone to $\varepsilon$-caprolactam is ammonium sulfate. Although the ammonium sulfate by-product is not wasted as it finds use as a fertilizer, it does decompose to sulfuric acid and subsequently acidifies soil and water sources.[662] While many research efforts have been devoted to reduce the formation of ammonium salt by-products, replacing the cyclohexanone feed by alternative sources could present more sustainable production opportunities.

An extremely promising sustainable feedstock due to its abundance is lysine. It is produced industrially as a side product of the fermentation of glucose, and 2.5 million metric tons were produced in 2016.[663] The ring closure step of lysine to $\alpha$-dimethyl amino caprolactam is fairly straightforward, but the subsequent removal of the amine in a simple, environmentally benign manner is more complex (Figure 51). However, Zhang and co-workers achieved both steps *via* a one-pot catalytic conversion using an Ir/HB-124 catalyst.[664] Nonetheless, the best achieved $\varepsilon$-caprolactam yield was 30%, which is far from ideal in the context of industrial manufacturing and shows that further improvement is needed.

$\varepsilon$-Caprolactam can also be synthesized from 6-aminocapronitrile, which in turn can be produced from butadiene, which can be derived from biomass.[665,666] Coote and co-workers used high-temperature water to hydrolyze the terminal nitrile on 6-aminocapronitrile to form 6-aminocaproic acid, which could then be ring closed to form $\varepsilon$-caprolactam. This method used water as a benign solvent and used a flow reactor method to generate a 90% $\varepsilon$-caprolactam yield with a calculated residence time of 96 seconds at 673 K and 400 bar. This route demonstrates a promising alternative to the traditional Beckmann rearrangement of cyclohexanone, but the sustainability of the conversion of butadiene into 6-aminocapronitrile is debatable, as a Michael reaction between 1,3 butadiene and hydrogen cyanide is required, followed by partial hydrogenation.[662]

5-Hydroxymethylfurfural has also been shown to be a feasible precursor for $\varepsilon$-caprolactam. Deuss and co-workers demonstrated the conversion of 5-hydroxymethylfurfural into 1,2,4-benzenetriol *via* a Lewis acid catalyzed rearrangement, which could then be deoxygenated to form cyclohexanone.[667] Nonetheless, the maximum yield of 1,2,4-benzenetriol was 55 mol % and metal catalysts, high temperatures, and high pressures were required to generate cyclohexanone, which then requires further transformation into $\varepsilon$-caprolactam. As previously mentioned in the section on caprolactone, Heeres and co-workers derived a method to also generate also caprolactam from 5-hydroxymethylfurfural. The latter being converted into $\varepsilon$-caprolactam in a 4-step-one-pot reaction (Figure 52).[549]

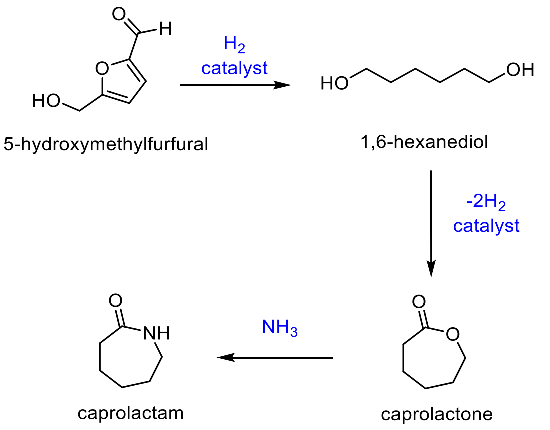


**Figure 52.** Synthesis of caprolactam from 5-hydroxymethylfurfural.

There are several promising routes toward the sustainable production of $\varepsilon$-caprolactam; however, currently they are somewhat hampered by less than desirable yields, high pressures and temperatures and rare earth catalysts. Perhaps the best course of action currently is to improve the current process of the Beckmann rearrangement of cyclohexanone and devise methods to generate cyclohexanone more sustainably.

### 4.2.2. 6-Membered Lactams.

The most well-known 6-membered lactam is $\delta$-valerolactam, which can be used to make nylons. The majority of synthetic routes to $\delta$-valerolactam *via* a bio-based sourced chemical are through the conversion of L-lysine into 5-aminovalerate, which can subsequently be ring-closed into the lactam. Generally this conversion is carried out metabolically by genetically engineered *E. coli*, of which there are three main methods (Figure 53).

The first method (Figure 53a) involves *E. coli* engineered to express DavA ($\delta$-aminovaleramidase) and (DavB L-lysine 2-monooxygenase) genes. DavB initially strips L-lysine of the amine in the 2-position and converts the carboxylic acid into an amide, which DavA then converts back into a carboxylic acid to form 5-aminovaleric acid. Examples in the literature have managed to generate yields of 20.8 g/L 5-aminovalerate from 30 g/L L-lysine in 12 h,[668] and 36.5 g/L from 60 g/L L-lysine in 24 h.[669] Another method incorporated an acyl-CoA ligase known as ORF-26 to ring close the 5-aminovalerate to generate 705 mg/L $\delta$-valerolactam from 10 g/L L-lysine.[670]

A second method (Figure 53b), which has been developed by Wendisch and co-workers, involves a three-step metabolic pathway.[671] First, L-lysine is decarboxylated with L-lysine decarboxylase to yield cadaverine, which is subsequently converted into 5-aminopentanal with the use of putrescine transaminase, followed by oxidation to the carboxylic acid with $\gamma$-aminobutyraldehyde. This method typically yields around 5 g/L of 5-aminovalerate when using shake flasks.[672]

Thirdly, L-lysine $\alpha$-oxidase can be used to oxidize the 2-position of L-lysine to form 6-amino-2-ketocaproic acid, which also generates hydrogen peroxide (Figure 53c). The $H_2O_2$ can then react with the 6-amino-2-ketocaproic acid to form 5-aminovaleric acid *via* an oxidative decarboxylation. In the method developed by Franssen and co-workers, the L-lysine $\alpha$-oxidase was immobilized on an epoxy activated solid support to give a synthesis method with 5-aminovaleric acid yields of up to 95%.[673] During the process, there is an equilibrium mixture, which could be influenced by pH to favor $\delta$-valerolactam at higher pH.[674] Furthermore, they managed to generate yields of 6.88 g/L of $\delta$-valerolactam from 40 g/L L-lysine.

Other bio-based chemicals other than lysine can be used for the production of $\delta$-valerolactam. For example, triacetic acid lactones can be biosynthesized from glucose.[675] These lactones can then be converted into lactams as demonstrated by Han and co-workers in 2021.[676] They initially reacted the lactone with ammonia to form 4-hydroxy-6-methylpyridin-2(1*H*)-one, which was then selectively transformed into 6-methylpiperidin-2-one with a Ru catalyst to give yields of up to 77%.

The production of sustainably sourced $\delta$-valerolactam is quite well developed, with L-lysine being an abundant natural feedstock. Moreover, the use of biochemistry means metal catalysts are not generally required, and harmful by-products are limited.

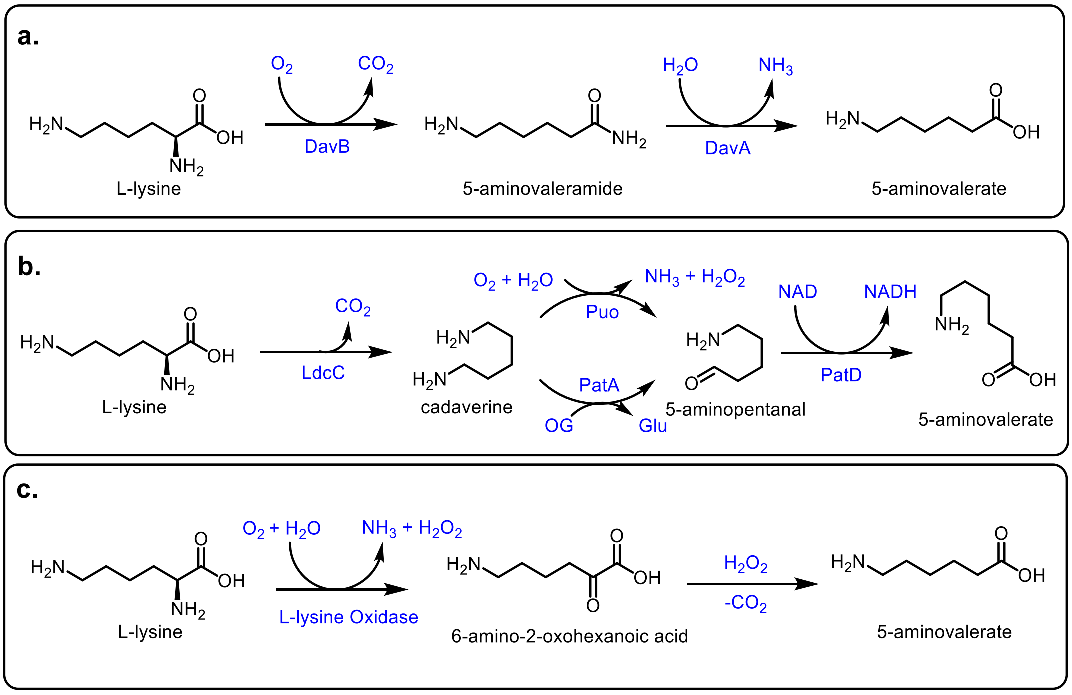


**Figure 53.** Three biological pathways to 5-aminovaleric acid.

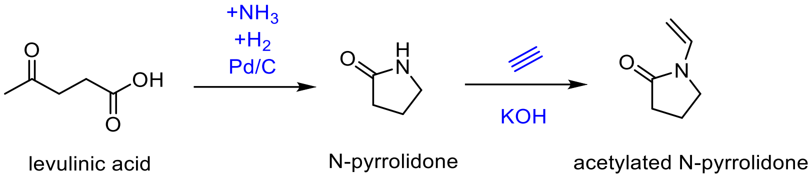


**Figure 54.** Production of acetylated *N*-pyrrolidones from levulinic acid.

**4.2.3. 5-Membered Lactams.** Butyrolactam, or 2-pyrrolidone, is the most basic 5-membered lactam, and can be functionalized *via* the R group on the nitrogen to yield materials with additional functionality.[677] The most common ways of generating butyrolactam sustainably tend to be from the platform chemical levulinic acid. The reductive amination of levulinic acid has been researched quite thoroughly, with both heterogenous and homogenous catalyst being investigated. An excellent heterogenous catalytic system was developed by Shimizu and co-workers, where they demonstrated the amination with a wide range of amines with generally high yields and no solvent.[678] Another example used Zr-Co catalysts prepared using chitosan as a carbon and nitrogen source to generate 5-methyl-2-pyrrolidone with a 93% yield.[679] Homogenous catalysts were first reported in 2011 with the use of a ruthenium catalyst and formic acid.[680] This was an effective method; however, it had the disadvantages of requiring high catalytic loading while displaying poor reactivity with bulky amines. In contrast, Fischmeister and co-workers developed a homogenous Iridium catalyst system using hydrogen as a proton source, which could tolerate bulky amines and required low catalyst loadings.[681] A catalyst-free system was developed in 2015 that could generate *N*-pyrrolidones with yields between 80% and 90%; however, temperatures up to 473 K were required.[682] An electrocatalytic approach was taken by Palkovits and co-workers, which has the advantage of being metal-free, and generates very good yields at temperatures between 80 and 150 °C, $H_2$ pressures of up to 5 MPa and within a 1−24 h reaction time.[683] Finally, 2-pyrrolidone synthesized from levulinic acid was functionalized by reaction with acetylene at 150 °C and 15 bar to generate vinyl monomers with yields of up to 82% (Figure 54).[684] These could then be polymerized through the vinylic groups and then subsequently ring-opened to form complex polymeric structures; however, one of the issues with the method is that the catalyst was not recoverable as the carbon support broke down.

As well as levulinic acid, other bio-based acids such as glutamic acid can be converted into butyrolactam. *γ*-Aminobutyric acid can easily be synthesized from glutamic acid, which can then be converted into *N*-methyl-2-pyrrolidone.[685] This can be done in a simple one-pot reaction with the use of methanol as a methylating agent in the presence of a halogen salt such as ammonium bromide. This particular method shows both high selectivity up to 90% and high conversions.[686] This method was also attempted with dimethyl carbonate as the methylating agent in the presence of a NaY zeolite; however, the selectivity was much lower at around 67%. To avoid the conversion step of glutamic acid into *γ*-aminobutyric acid, glutamic acid can be directly converted into various *N*-alkyl-2-pyrrolidones in a one-pot reaction.[687] First, the amine is reacted with a ketone and subsequently reduced under mild conditions with a palladium catalyst, and the subsequent product is ring closed followed by decarboxylation at 250 °C with a $Pd/Al_2O_3$ catalyst. This route does provide reasonable

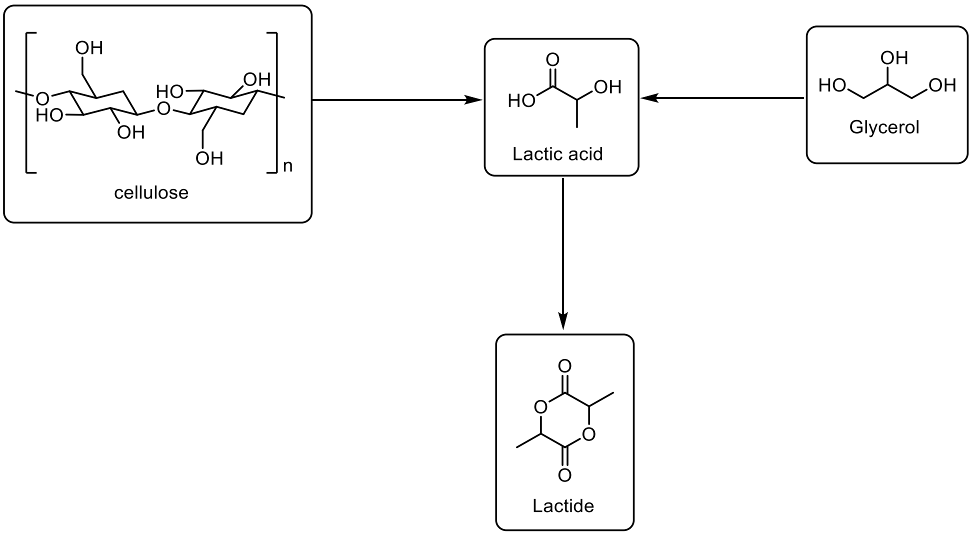


**Figure 55.** Sources of bio-based and sustainable lactides.

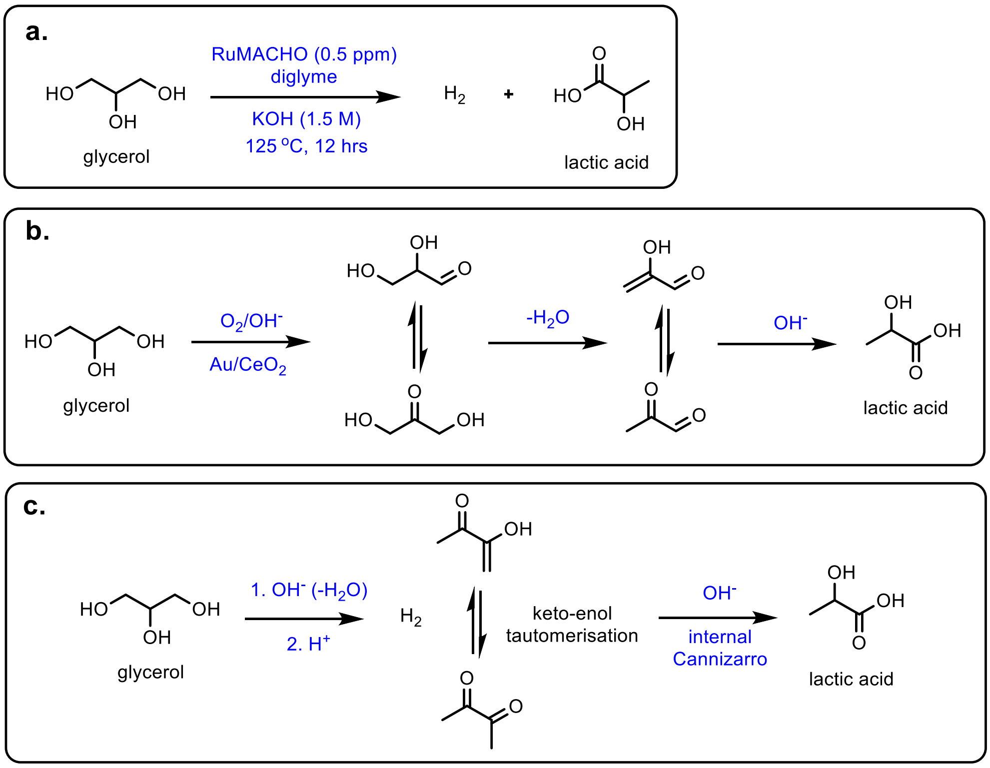


**Figure 56.** Use of RuMACHO for dehydrogenation of glycerol (a). Au nanoparticles on $CeO_2$ for lactic acid production (b). Hydrothermal conversion of glycerol into lactic acid (c).

yields but also requires metal catalysis and high temperatures, which detract from the sustainable aspect of the route.

Finally, butyrolactam has been synthesized from 4-aminobutyric acid *via* a metabolic pathway using engineered *E. coli*. Titers could be produced of up to 54 g/L and other lactams such as caprolactam and valerolactam were also possible but at not as high a titer.[688]

The variety of sustainable precursors for lactam synthesis is not as well developed as for lactones. However, L-lysine stands out as being a very promising feedstock as it is abundant in nature and can be transformed into $\varepsilon$-caprolactam and $\delta$-valerolactam. Although polyamides are very robust and durable polymers, they are also much more difficult to degrade than polyesters and so reside in the environment for extended periods.

### 4.3. Lactides

Polylactic acid (PLA) is perhaps one of the most promising biodegradable, biocompatible and renewable polymeric materials in today's polymer landscape. These attributes of PLA make it suitable for a range of applications such as inkjet printing,[689] tissue engineering[690] and bone fixation.[691] Although PLA can be produced from lactic acid, several disadvantages are associated with this direct polymerization, including difficulty reaching high monomer conversion, side

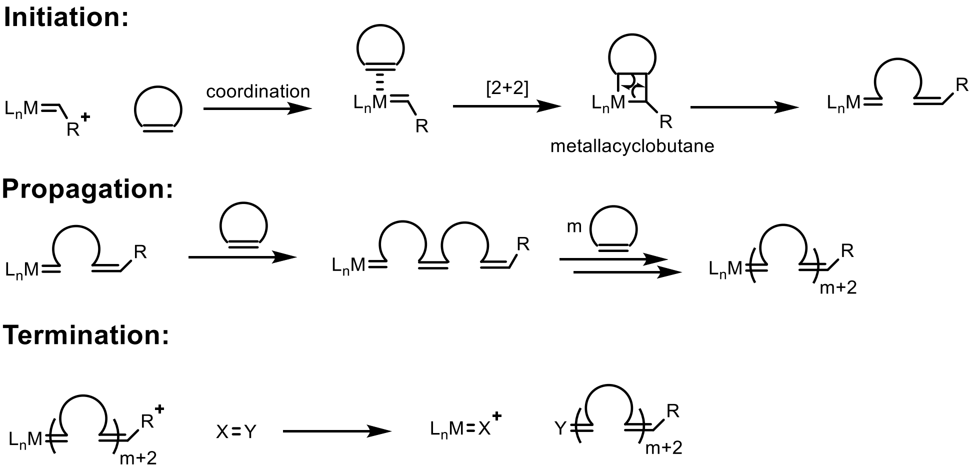


**Figure 57.** General mechanism for ring-opening metathesis polymerization (ROMP).

reactions such as intermolecular transesterifications, and racemization between L-lactic acid and D-lactic acid.[692] Alternatively, lactic acid can be converted into the cyclic lactide intermediate, which can be subjected to ring-opening polymerization, thereby allowing for the formation of PLA is a very controlled manner with high molecular weights and low dispersities.[693] In the following, we will focus the discussion on the synthesis of lactic acid from renewable sources, as virtually all lactide is synthesized from lactic acid (Figure 55).

As of 2018, the global lactic acid market was valued at \$2.9 billion, and is expected to grow to between \$8 and \$10 billion by 2025.[694] Currently, the majority of lactic acid is produced *via* the fermentation of carbohydrates; however, this route has several disadvantages including long fermentation times, low substrate concentration and complicated purifications.[695] There are three main chemical synthesis routes to convert glycerol into lactic acid, i.e., dehydrogenation, selective oxidation and hydrothermal conversion.

Glycerol can be dehydrogenated to generate lactic acid and hydrogen gas by means of a technique developed by Cole-Hamilton and co-workers in 1988 using a $RuH_2N_2(Ph_3P)_3$ catalyst.[696] This method was primarily developed for hydrogen generation, but has been further developed by making use of a RuMACHO (RuHCl(PNPPh)CO) catalyst (Figure 56a). Using this catalyst, complete conversion of glycerol with 67% lactic acid yield was realized.[697]

Selective oxidation can be used to generate a variety of oxygenated products from glycerol including lactic acid (Figure 56b). Several catalysts such as $CeO_2$ supported gold nanoparticles and Pt/activated carbon[698,699] generate high yields of lactic acid, but require basic catalysts that result in further purification steps to obtain lactic acid. Fan and co-workers developed a Pt/Sn-MFI catalyst that could generate lactic acid from glycerol with a selectivity of 81% and a conversion of 90%. Furthermore, the route does not require a base, implying a greener synthesis route than traditional oxidative routes of lactic acid.[700]

Hydrothermal conversion is a good technique for obtaining low molecular weight organic acids, and the generation of lactic acid from glycerol is a good example of this (Figure 56c). Yields of up to 90% have been reported previously using a basic solution of 0.33 M glycerol. However, such a low substrate concentration is a major disadvantage for an industrial viable process.[701] Since then, the process has been improved to give a lactic acid yield of ~80% when using an initial glycerol concentration of 2.5 M.[702]

Cellulose is another common precursor for lactic acid, and the transformation from cellulose to lactic acid involves three distinct steps. First, cellulose is hydrolyzed into glucose using a Brønsted acid. The glucose is then isomerized into fructose, which is then converted into lactic acid *via* a retro-aldol reaction. The conversion of glucose into lactic acid requires a catalyst with Lewis acidity, of which $Ba(OH)_2$ has been shown to be a promising example, showing a lactic acid yield of 95% after 48 h from treatment of glucose under anaerobic conditions. Nevertheless, this method requires low substrate concentrations to achieve high conversions resulting in an issue for any potential industrial interest.[703] Various other soluble Lewis acid salts have been used, including $Pb^{2+}$, $VO^{2+}$, $Er^{3+}$ and $Al^{3+}/Sn^{2+}$.[704−707] $Pb^{2+}$ has been shown to be able to convert ball-milled cellulose into lactic acid with a 68% yield; however, the toxicity of the salt can be problematic.[704] $ErCl_3$ is an extremely promising catalyst, showing a quantitative conversion of cellulose with 91% yield of lactic acid; however, this method is hampered by low substrate concentrations.[706]

One of the main issues with using homogenous Lewis acid salts is the difficulty in purifying them, which gives heterogenous catalysts an advantage industrially. An Erbium exchanged montmorillonite K10 was developed as a heterogenous catalyst by Dong and co-workers that could transform cellulose with 100% conversion, with a lactic acid yield of up to 68%. However, the catalyst was shown to undergo structural changes upon recycling resulting in decreased catalytic performance.[708] To build on this, Lappas and co-workers developed a *p*-toluenesulfonic acid (TSA)/$SiO_2$-$Al_2O_3$ catalyst that demonstrated a selectivity of 38% toward lactic acid, with a yield of 24%. Importantly, the catalyst was shown to be reusable for at least 3 reaction cycles.[694]

### 4.4. Cyclic Olefins for Ring-Opening Metathesis Polymerization

Ring-opening metathesis polymerization (ROMP) is a type of olefin metathesis reaction that uses relief of ring strain as its driving force. ROMP has increased in popularity since the 1950s because of the development in its mechanistic understanding, leading to well-defined catalysts and consequently polymers with more complex architectures.[709] One of the most important features of olefin metathesis reactions is that any unsaturation present in the monomer is retained in

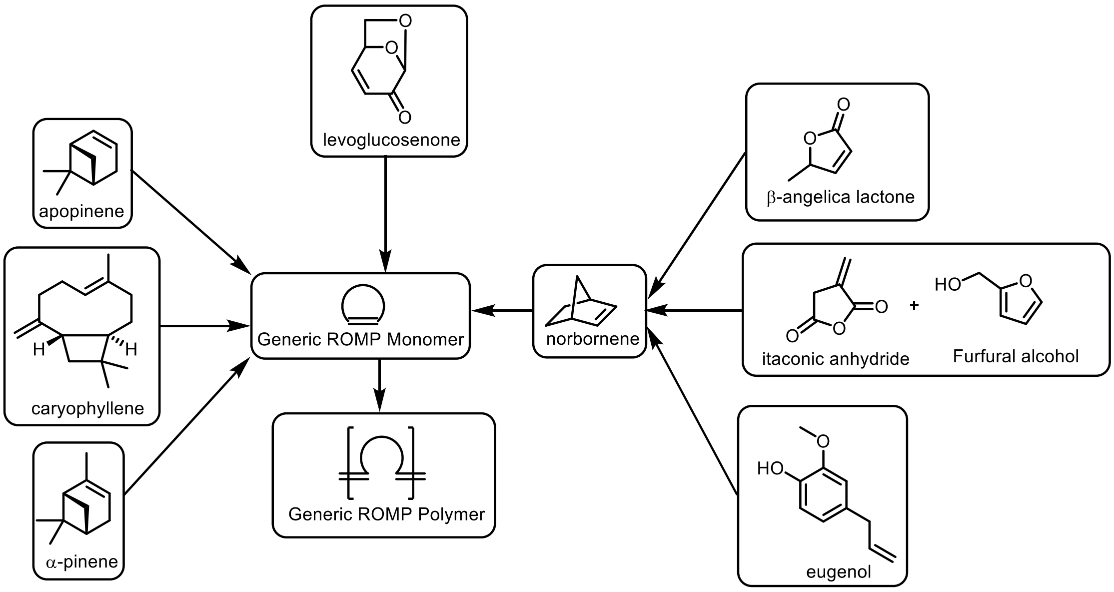


**Figure 58.** Sources of bio-based, sustainable monomers for ROMP.

the polymer. Common catalysts for ROMP are transition metal alkylidene complexes, which undergo a [2+2] cycloaddition with the cyclic olefin to form a metallacyclobutane, followed by a cycloreversion to produce a new metal alkylidene (see Figure 57 for general ROMP mechanism). This process repeats until all the monomer is consumed or a termination event takes place. In this section, cyclic olefin monomers that are susceptible to ROMP and are derived from sustainable sources will be discussed.

Suitable monomers for ROMP require cyclic structures with an internal double bond, and these types of structures can be found naturally as terpenes. Indeed, research into terpenes such as *α*- and *δ*-pinene for ROMP is already prevalent and we will first begin by discussing monomers derived from them (Figure 58).

Terpenes make up a large market, with around 350 kilotons being harvested per annum. Generally, *α*-pinene is the major volatile component making up between 45-97% of pine sap. *α*-Pinene contains an internal double bond that is rather sterically hindered, making its polymerization difficult. For this reason, *α*-pinene is normally transformed into better polymerizable monomers such as *δ*-pinene or apopinene (Figure 59).

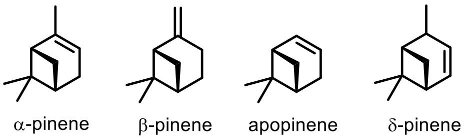


**Figure 59.** Chemical structures of pinene derivatives.

Apopinene can be synthesized by allylic oxidation of *α*-pinene with $SeO_2$ followed by decarbonylation with Pd/$BaSO_4$. Using a 3rd generation Grubbs catalyst, apopinene can be polymerized to yield polymers of up to 16 kDa and dispersity values as low as 1.6.[710] An alternative route to make use of *α*-pinene is by converting it into *δ*-pinene, which has previously been realized in a 3-step process followed by a distillation step.[711] The resulting polymers in this case had $M_n$ values of 70 kg/mol and low dispersity values of around 1.2. Both of these methods highlight the potential for pinenes to act as bio-based precursors for monomer synthesis; however, the synthetic routes are far from sustainable. Moreover, the distillation step in the *δ*-pinene requires reaction of *α*-pinene with chlorosulfonyl isocyanate to create a boiling point disparity between the pinenes to allow for distillation. To remove this difficulty, Kennemur and co-workers investigated the effect of *α*-pinene acting as a co-solvent during the polymerization of *δ*-pinene.[712] They discovered that the polymerization of *δ*-pinene was still effective as long as the molar ratio of *α*-pinene to the 3rd generation Grubbs catalyst did not exceed 40:1.

Caryophyllene is a sesquiterpene that makes up about 10% of clove oil and is generally burned as a waste product. However, caryophyllene contains a cyclobutene moiety and an exocyclic double bond, resulting in a structure with excellent potential for further transformation. Poly(caryophyllene) can be made with molecular weights of up to 20 000 g/mol with dispersity values of 1.8−1.9 with a generation III Grubbs catalyst.[713] Furthermore, the exocyclic bonds present in poly(caryophyllene) can be cross-linked by various chemical strategies (e.g., thiol−ene reaction) to generate polymers with storage moduli between 1 and 100 MPa and an elongation until break of up to 360%.[714]

Norbornenes are the monomer of choice for ROMP due to their commercial availability, ease of synthesis and polymerisability.[715] Although norbornene is generally produced by the Diels−Alder reaction between ethylene and cyclopentadiene, other bio-based structures can be used instead. For example, a very interesting route was developed by North *et al.* where they attempted to form an ester between itaconic anhydride and furfuryl alcohol.[716] However, the reaction gave an oxanorbornene-lactone ring as a single product instead (Figure 60). The

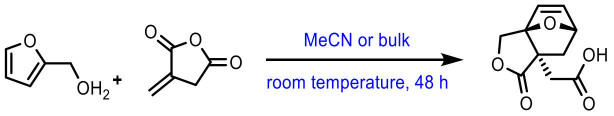


**Figure 60.** Oxanorbornene-lactone ring formation from itaconic anhydride and furfuryl alcohol.

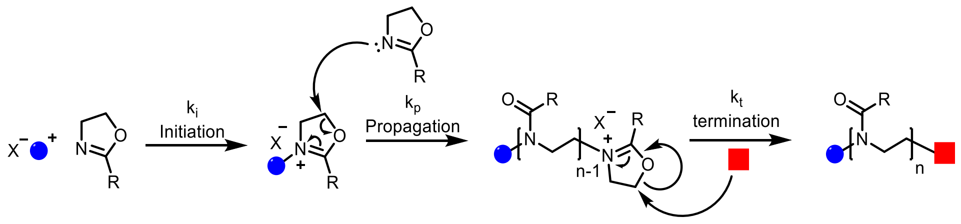


**Figure 61.** General mechanism of the cationic ring-opening polymerization of 2-oxazolines.

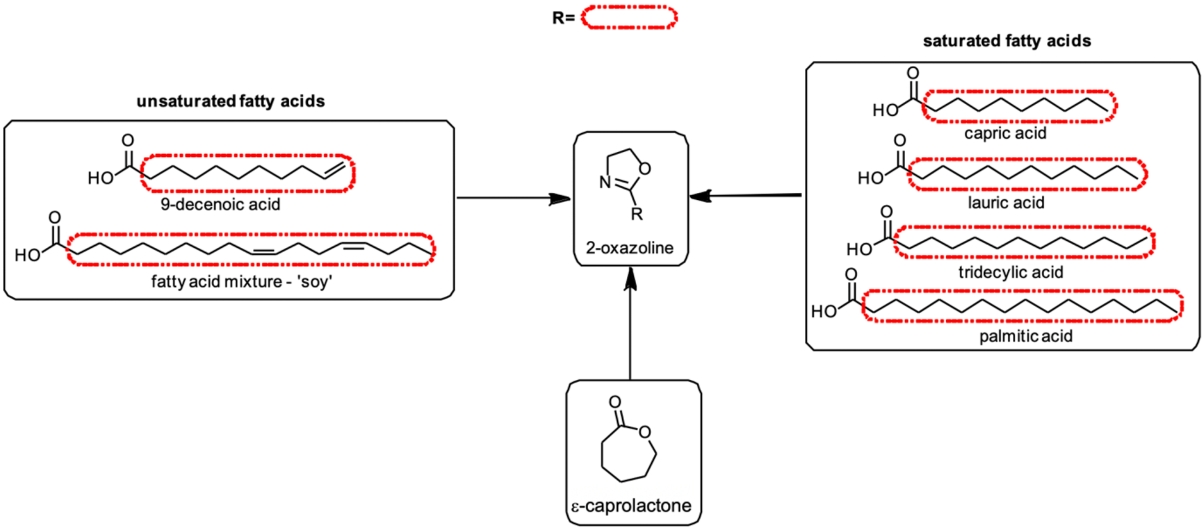


**Figure 62.** Sources of bio-based, sustainable 2-oxazoline monomers.

reaction proceeded without the need for solvents or catalysts and was 100% atom economical, highlighting a potential monomer with definite green credentials. The subsequent polymers were then used to prepare a range of different esters and tertiary amides. After reaction optimization, polymers were made with monomer conversions of up to 93% and $M_n$ values of 23.5 kDa. Polymers synthesized had glass transition ($T_g$) values in the range of 115−203 °C and thermal decomposition temperatures above 300 °C.[717]

Norbornenes can also be synthesized by the Diels−Alder reaction between cyclopentadiene and other double bond containing compounds, thereby broadening the monomer substrate scope. For example, Fang and co-workers performed a Diels−Alder reaction between cyclopentadiene and a fluorinated eugenol derivative to generate high molecular weight, well controlled polymers with potential application in the microelectronic industry.[718] As well as eugenol, angelica lactones can be combined with cyclopentadiene to generate norbornene derivatives that could then be polymerized to form polymers with $M_n$ values of up to 122 kDa. However, obtaining pure $\beta$-angelica lactone can be challenging.[719]

Norbornene can also be functionalized and subsequently polymerized to generate useful materials. Notable examples include the esterification of 5-norbornene-2-methanol with various fatty acids, followed by polymerization to generate polymers with glass transition temperatures that span a large temperature range, i.e., from −32 to +102 °C.[715]

Next to terpenes and norbornenes, levoglucosenol can also be used as a bio-based monomer source for ROMP. Levoglucosenol can be derived from the reduction of levoglucosenone, which in turn is generated from the pyrolysis of cellulose. The reduction step can be carried out simply with sodium borohydride, and the subsequent polymerization yielded polymers with high molecular masses that were shown to be degradable, highlighting a promising polymeric system that is bio-based and degradable.[720]

## 4.5. 2-Oxazolines

Poly(2-oxazoline)s are a versatile class of polyamide that are structurally analogous to polypeptides and thus can be regarded as pseudo-peptides. Poly(2-oxazoline)s are synthesized *via* the cationic ring-opening polymerization of 2-oxazoline ring structures (Figure 61), which was first carried out in the 1960s.[721] One of the main benefits of the cationic ring-opening polymerization of 2-oxazolines is the degree of flexibility associated with this chemistry, which can be used to make complex polymeric architectures.

2-Oxazolines can easily be synthesized from carboxylic acids *via* one of three main routes.[722] First, nonactivated carboxylic acids are reacted with ethanolamine to form the associated amide, followed by the subsequent catalyzed ring closure. The second route is known as the Witte-Seeliger method and involves conversion of a carboxylic acid to a nitrile followed by transformation into a 2-oxazoline. The third method is known as the Wenker method, where a carboxylic acid is coupled with chloroethylamine, which then undergoes ring closure with a solution of potassium hydroxide.

The majority of literature procedures on the sustainable synthesis of poly(2-oxazolines) is based on using fatty acids as a renewable feedstock (Figure 62). The resultant monomers therefore contain saturated and unsaturated hydrocarbon groups and thus are not particularly structurally diverse. However, the polymeric structures formed with 2-oxazolines derived from fatty acids have interesting physical properties such as low surface energies and high crystallinity.[723]

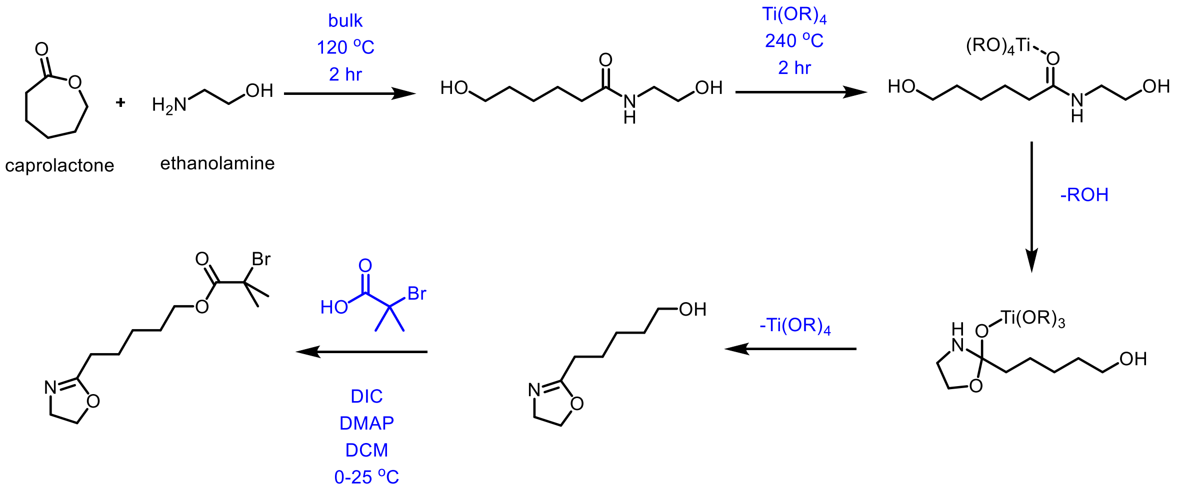


**Figure 63.** Formation of 2-oxazoline "inimer" and subsequent polymerization.

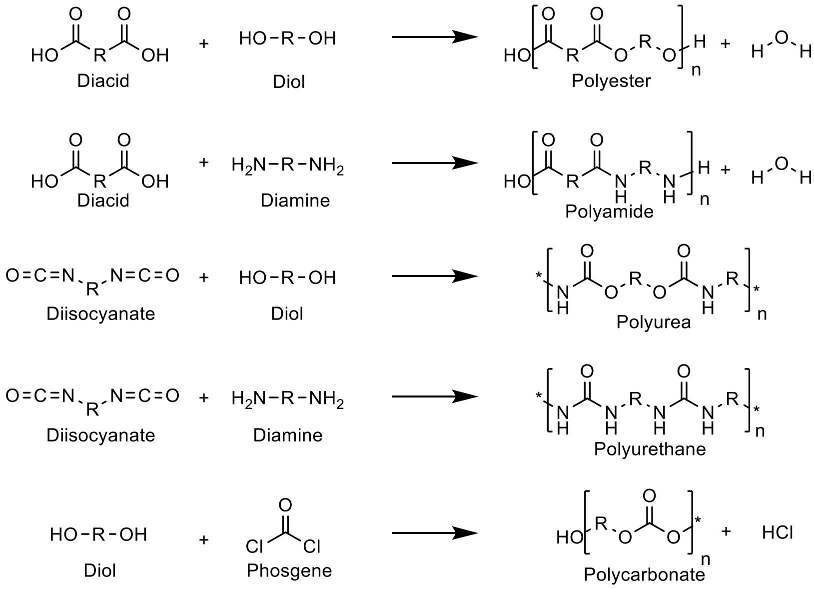


**Figure 64.** General reaction schemes for the conventional synthesis routes of common step-growth polymer classes, derived from difunctional monomers.

Nonetheless, unsaturated fatty acids can provide a route to further functionalization, as was demonstrated by Schubert and co-workers when they synthesized a 2-oxazoline from the sustainably derived fatty acid decenoic acid.[724] The pendant double bond allowed for further modification that was realized by the thiol−ene addition reaction between the synthesized polymer and a thiolated glucose moiety. As well as glycosylation, other previous examples of functionalization of these double bonds include epoxidation, hydroboration, and hydrosilylation.[725,726]

Differing from the majority of sustainable 2-oxazoline research, Becer and co-workers derived a functional monomer from caprolactone by using ethanolamine and a Lewis acid, notably the same chemicals that can be used to create 2-oxazolines from fatty acids (Figure 63). Their approach led to a monomer with pendant hydroxyl groups that could then undergo subsequent transformation. This was illustrated by grafting on an initiator for Cu(0)-mediated reversible-deactivation radical polymerization (RDRP) to form an "inimer", and then polymerizing said inimer to form a poly(2-oxazoline) backbone with acrylate brushes.[727]

## 5. BISFUNCTIONAL MONOMERS USED IN THE SYNTHESIS OF COMMODITY THERMOPLASTICS

Step-growth polymerization is a class of polymerization wherein monomers bearing functionalities greater than 1 polymerize in a sequential manner, first forming di-, tri- and oligomers, and eventually long polymer chains. The polymerizations can either occur between two monomers bearing multiple of the same functional group (AA + BB type), or from a single monomer bearing two different functional groups (AB-type). Homo-difunctional compounds are typically easier to access than hetero-difunctional compounds and hence AA + BB type step-growth polymerizations are more commonly utilized, with the conventional synthesis of 5 major AA+BB step-growth polymer classes (i.e., polyester, polyamide, polyurea, polyurethane and polycarbonate) shown in Figure 64.

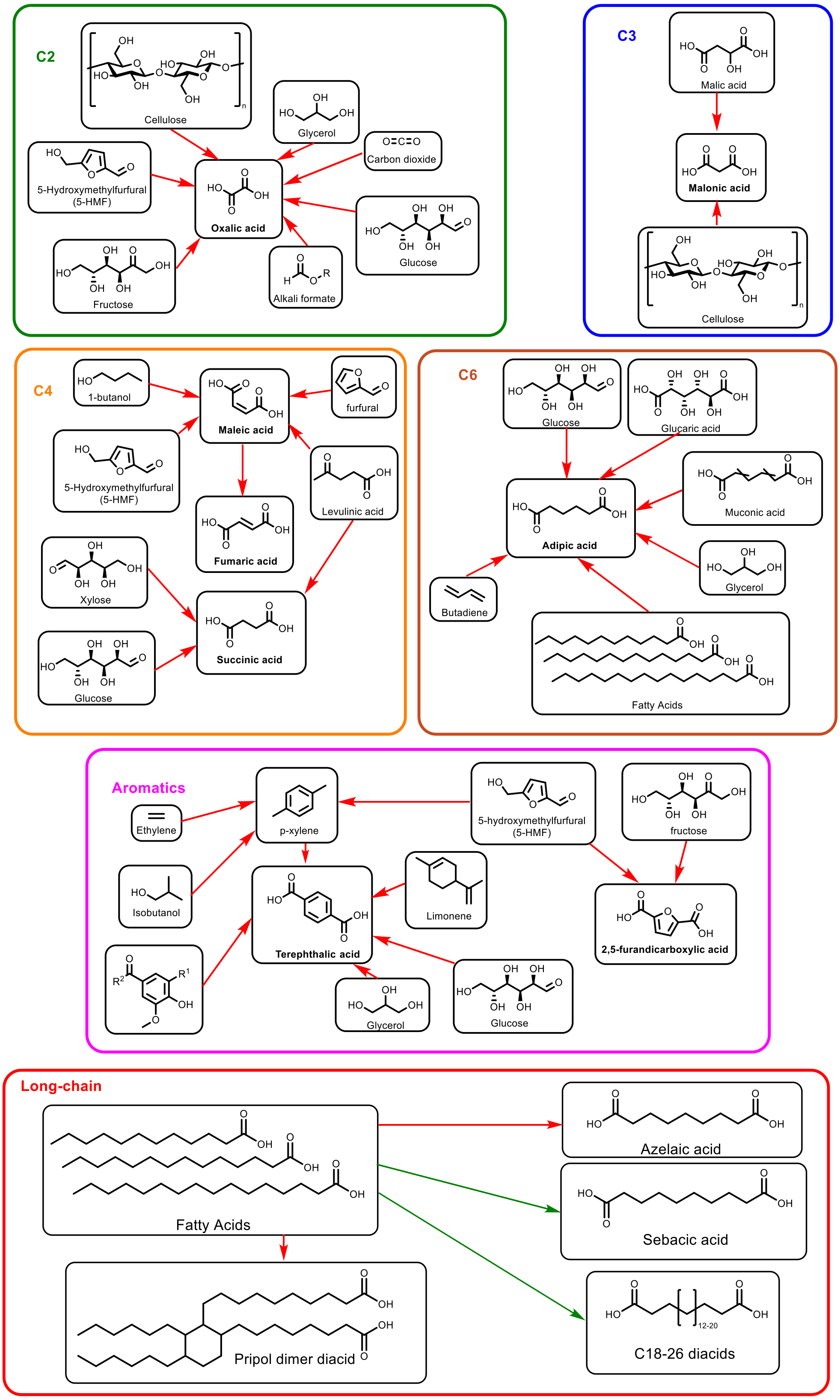


**Figure 65.** Summary of the routes to various dicarboxylic acids from biomass sources.

The polymer class produced *via* step-growth polymerization is determined directly by the combination of their respective monomer classes, with diacids, diols, diamines, diisocyanates and phosgene commonly used. Unlike the previous sections, which largely pertain to homopolymers made from single monomers, this section focusing on AA+BB step-growth necessitates multiple monomers for each polymer. In exploring routes from biomass to these step-growth polymers, the focus

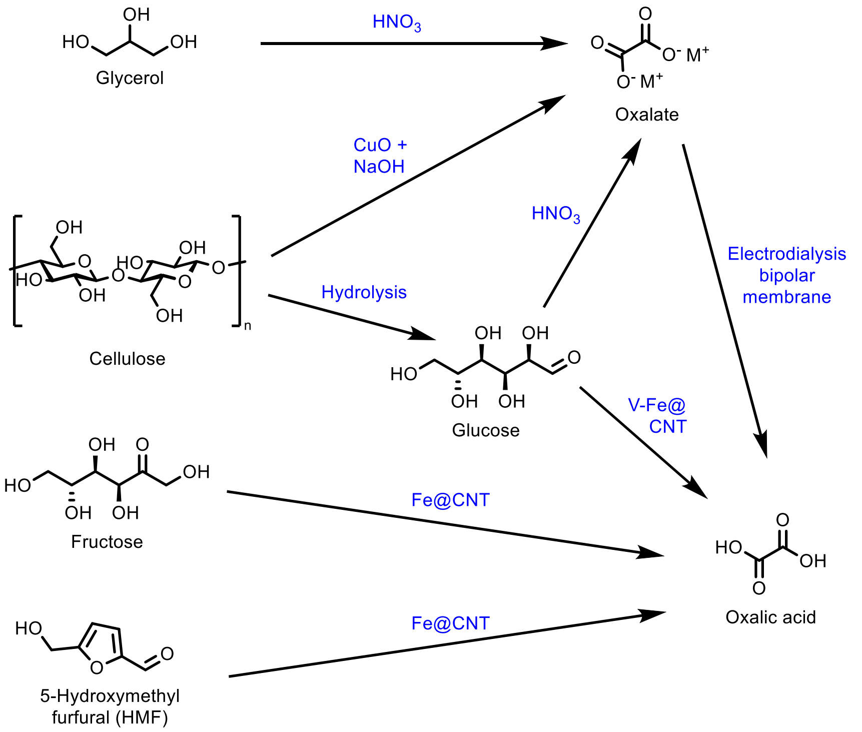


**Figure 66.** Routes to oxalic acid from sustainable biomass sources, excluding $CO_2$ and CO.

must be on the production of these key monomer classes, such that existing polymerization techniques can be used to transform renewable step-growth building blocks into the desired conventional polymer products.

## 5.1. Bifunctional Monomers

### 5.1.1. Diacids.

**5.1.1. Diacids.** Diacids (dicarboxylic acids) are crucial for the synthesis of several key polymer types, including polyesters and polyamides. The wide availability, ease of synthesis and relative stability of acid moieties have enabled the preparation of a wide range of diacid compounds, although the scope of this review focuses on preparing $\alpha,\omega$-diacids, as these are the most industrially relevant diacid isomers (Figure 65).

*5.1.1.1. C2 Diacid.* Oxalic acid (OA, 1,2-ethanedioic acid) was discovered in 1734 and is currently used on a large scale in the pharmaceutical, agricultural, chemical and textile industries.[728] Alongside its potential for use in step-growth polymerization, selective reduction of OA can yield several other commercially useful derivatives, including glyoxylic acid, glycolic acid, glyoxal, glycol aldehyde and ethylene glycol.[728] OA is currently predominantly produced from coal-derived fossil naphtha, but routes to OA from several biomass feedstocks have been developed, including cellulose, ethanol, glycerol, glucose and other $C_6$ substrates such as fructose and 5-hydroxymethlyfurfural (5-HMF), as well as from $CO_2$ (Figure 66, Table 18).[729−731]

Cellulose can be converted to OA in two ways, *via* hydrolysis to glucose followed by nitric acid oxidation, or *via* direct immersion of cellulose in an alkaline solution (Figure 66).[732−734] A series of catalysts have been used to optimize the second pathway, with a CuO catalyst in aqueous NaOH at 200 °C giving OA with a yield of 41.5%, through several organic intermediates (Table 18, entry 1).[735,736] The conversion of glycerol to OA was investigated by Xu and co-workers with an Au/$CeO_2$ catalyst in aqueous NaOH, giving 55% yield of OA at 98% glycerol conversion (Table 18, entry 2).[737] Notably, in both the cellulose pathways and the glycerol pathway, the alkali conditions produce oxalate, which must then be acidified to OA, generating large amounts of waste.[731] A base-free conversion of fructose, glucose, and 5-HMF directly to OA has been achieved by using Fe@CNT and V-Fe@CNT catalysts (Table 18, entries 3−5).[738] Moderate OA yields (46−49%) were obtained with the only major side products being succinic and formic acid, two other valuable organic acids. The lack of selective and sustainable processes for the hydrolysis of cellulose must be overcome to continue developing carbohydrate-derived OA.[731]

$CO_2$ and CO are frequently overlooked feedstocks for industrial synthesis and can be converted to OA in multiple ways, as was recently discussed in depth by Schuler *et al.*[728] Therein, the most sustainable and practical routes identified for near-future commerciality are described briefly (Figure 67). For example, the direct conversion of $CO_2$ to OA is possible *via* electrochemical reduction with metals, electrochemical reduction with metal complexes, and reduction with sacrificial calcium ascorbate. In the electrochemical reduction with metals, the absence of water is critical to prevent competing side-reactions and give high OA production.[739−741] The zinc oxalate process, which utilized a sacrificial zinc anode, benefitted from the absence of side products and precious metal requirements.[742] Although calculated to be price competitive on a 2 Mt scale, the process is limited by the requirement for dry solvents and has never been tested on a continuous closed-loop pilot scale. Recently, thin films of glassy carbon coated with $Cr_2O_3$ /$Ga_2O_3$ in aqueous conditions gave a 59% yield of oxalate (Figure 67, Table 18, entry 6).[743]

Electrochemical reduction with metal complexes suffers from complex systems, long reaction times, and toxic solvents, but benefits from high selectivity and the possible use of non-precious metals.[744] A wide range of metal complexes have been

Table 18. Catalysts, Conditions and Yields for the Production of Selected Diacids and Important Intermediates from Biomass Sources

| Entry | Target | Feedstock | Catalyst | Temperature (°C) | Pressure (bar) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | OA | Cellulose | CuO (+base) | 200 | 3 ($O_2$) | 100 | 42 | 42 | 735 |
| 2 | OA | Glycerol | Au/$CeO_2$ (+base) | 60 | 3 ($O_2$) | 98 | 56 | 55 | 737 |
| 3 | OA | Fructose | Fe@CNT | 140 | 10 ($O_2$) | 99 | 47 | 46 | 738 |
| 4 | OA | Glucose | V-Fe@CNT | 150 | 20 ($O_2$) | 97 | 48 | 46 | 738 |
| 5 | OA | 5-HMF | Fe@CNT | 140 | 10 ($O_2$) | 99 | 49 | 48 | 738 |
| 6 | OA | $CO_2$ | $Cr_2O_3$/$Ga_2O_3$@C | 25 | n/a | n/a | n/a | 59 | 743 |
| 7 | OA | K-formate | KH | 190 | 1 (Ar) | n/a | n/a | 97 | 744 |
| 8 | MalonA | Cellulose | NaOH | 300 | n/a | n/a | n/a | 40 | 769 |
| 9 | MalonA | Malic acid | $H_5[PMo_{10}V_2O_{40}]$ | 100 | 10 ($O_2$) | 99 | 69 | 68 | 770 |
| 10 | MalA | Furfural | V-oxides | 320 | 0.05 ($O_2$) | 100 | 70 | 70 | 771 |
| 11 | MalA | Furfural | $H_3PMo_{12}O_{40}$ | 110 | 20 ($O_2$) | 50 | 69 | 35 | 772 |
| 12 | MalA | Furfural | Ti-$SiO_2$ @ Zeolite | 120 | n/a | 99 | 72 | 71 | 773 |
| 13 | MalA | Furfural | BHC | 100 | n/a | 100 | 61 | 61 | 774 |
| 14 | MalA | Furfural | Formic acid | 60 | n/a | n/a | n/a | 95 | 775 |
| 15 | MalA | 5-HMF | $Fe_3O_4$@$SiO_2$ | 110 | 10 ($O_2$) | 36 | 85 | 31 | 776 |
| 16 | MalA | 5-HMF | Formic acid | 100 | n/a | n/a | n/a | 89 | 775 |
| 17 | MalA | 1-Butanol | Vanadyl pyrophosphate $(VO)_2P_2O_7$ | 340 | 1 (Air) | n/a | 39 | n/a | 777 |
| 18 | MalA | LevA | $VO_xSiO_2$ | 300 | n/a ($O_2$) | 100 | 71 | 71 | 778 |
| 19 | FA | MA | P(4-vinylpyridine) | 200 | n/a | n/a | n/a | 78 | 779 |
| 20 | FA | MA | No catalyst | 200 | n/a | n/a | n/a | 72 | 779 |
| 21 | SA | Xylose | $SO_3H$-CD | 60 | n/a | 100 | 81 | 81 | 780 |
| 22 | SA | LevA | Ru(III)@MNP, $H_2O_2$ | 150 | 14 ($O_2$) | 79 | 99 | 78 | 781 |
| 23 | SA | LevA | Trifluoroacetic acid | 90 | n/a | 100 | 62 | 62 | 782 |
| 24 | SA | Glucose | Ru/$NH_2$-rGO | 161 | 18 ($O_2$) | 100 | 87 | 87 | 783 |
| 25 | SA | HMF | Ru-$FeO_3$@$SiO_2$=CoOx | 110 | 10 ($O_2$) | 90 | 81 | 73 | 776 |
| 26 | SA | Fructose | Fe@CNT | 140 | 10 ($O_2$) | 99 | 21 | 21 | 738 |
| 27 | AA | Butadiene | Pd(II)/Rh(III) | 120 | 50 (CO) | n/a | n/a | 96 | 784 |
| 28 | AA | SA | 1) Pd-Re/$TiO_2$, 2)Rh $(PPh)_3$COCl | 1) 200<br>2) 175 | 1) 69 ($H_2$)<br>2) 48 (CO) | 1) 99<br>2) 100 | 1) 86<br>2) 74 | 1) 85<br>2) 74 | 785 |
| 29 | AA | GA | Pd-Rh/Davisil 635 | 140 | 49 ($H_2$) | n/a | n/a | 89 | 786 |
| 30 | AA | MucA | Pt/C | 24 | 24 ($H_2$) | n/a | n/a | 97 | 787 |
| 31 | *p*-Xylene | Ethylene | 1) Ir-based<br>2) no catalyst<br>3) 400 | 1) 190<br>2) 250<br>3) Pt/$Al_2O_3$ | 1) n/a<br>2) 41 ($C_2H_4$)<br>3) n/a | n/a | n/a | 89 | 788 |
| 32 | *p*-Xylene | Isobutanol | 1) $Al_2SiO_3$<br>2) $Al_2SiO_3$<br>3) CrOx/$Al_2O_3$ | 1) 327<br>2) 327<br>3) 527 | n/a | n/a | n/a | 63 | 789 |
| 33 | *p*-Xylene | Dimethyl furan | $ZrO_2$ | 275 | 40 ($C_2H_4$) | 99 | 90 | 89 | 790 |
| 34 | TPA | Lignin oil | 1) $MoO_x$/AC<br>2) $Pd(OAc)_2$<br>3) Cu/Mn$(OAc)_2$ + KBr | 1) 320<br>2) 25<br>3) 120 | 1) 30 ($H_2$)<br>2) n/a (CO)<br>3) 10 ($O_2$) | n/a | n/a | 15 | 791 |
| 35 | TPA | Glucose + glycerol | 1)$TiCl_4$<br>2)Pd/C<br>3) Co-Mn$(OAc)_2$ | 1) 25<br>2) 100<br>3) 100 | 1) n/a<br>2) n/a<br>3) 1($O_2$) | n/a | n/a | 68 | 792 |
| 36 | TPA | Limonene | 1) $FeCl_3$<br>2) $MnO_x$-$FeO_x$ | 1) 50<br>2) nr | 1) n/a ($N_2$)<br>2) n/a | n/a | n/a | 85 | 793 |
| 37 | FDCA | HMF | Pt/N-doped-C | 110 | 10 ($O_2$) | 100 | 99 | 99 | 794 |
| 38 | FDCA | HMF | $Pt_5Bi_1$/C | 100 | 40 (air) | 100 | >99 | >99 | 795 |
| 39 | FDCA | HMF | Pd/HT | 100 | n/a ($O_2$) | 100 | 92 | 92 | 796 |
| 40 | FDCA | HMF | $Fe_2O_3$@HAP-Pd(0) | 100 | n/a ($O_2$) | 97 | 96 | 93 | 797 |
| 41 | FDCA | HMF | Au/HY | 60 | 3 ($O_2$) | 100 | >99 | >99 | 798 |
| 42 | FDCA | HMF | Au/$Ce_{0.9}Bi_{0.1}O_2$ | 65 | 10 ($O_2$) | 100 | >99 | >99 | 799 |
| 43 | FDCA | HMF | $Au_3Pd_2$/La-CaMgAl-LDH | 120 | 5 ($O_2$) | 100 | 100 | 100 | 800 |
| 44 | FDMC | HMF | Au/$CeO_2$ | 130 | 10 ($O_2$) | 100 | >99 | >99 | 801 |
| 45 | FDCA | HMF | Ru/C | 110 | 10 ($O_2$) | 100 | 97 | 97 | 802 |
| 46 | FDCA | HMF | Ru/$MnCo_2O_4$ | 120 | 24 ($O_2$) | 100 | 99 | 99 | 803 |
| 47 | FDCA | HMF | CuO-$MnO_2$-$CeO_2$ | 130 | 20 ($O_2$) | 99 | 99 | 98 | 804 |

**Table 18. continued**

| Entry | Target | Feedstock | Catalyst | Temperature (°C) | Pressure (bar) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 48 | FDCA | HMF | $Co_3O_4$-$Mn_{0.2}CoO$ | 140 | 1 ($O_2$) | 100 | >99 | >99 | 805 |
| 49 | FDCA | HMF | $CoO_x$-mesoporous C | 80 | 5 ($O_2$) | 98 | 97 | 95 | 806 |
| 50 | FDMC | HMF | Co@CN | 80 | 1 ($O_2$) | 100 | 95 | 95 | 807 |
| 51 | FDCA | HMF | N-doped nanoporous C | 80 | n/a ($O_2$) | 100 | 80 | 80 | 808 |
| 52 | FDCA | Fructose | Pd/CC | 100 | n/a ($O_2$) | 91 | 70 | 64 | 809 |
| 53 | FDCA | Fructose | Amberlyst-15, Ru/C | 110 | 40 ($O_2$) | n/a | n/a | 65 | 810 |
| 54 | FDCA | Fructose | FDCA, Pt/C | 110 | 40 ($O_2$) | n/a | n/a | 65 | 811 |
| 55 | FDCA | Fructose | Amberlyst-15, AuPd/HT | 95 | n/a ($O_2$) | n/a | n/a | 78 | 812 |
| 56 | FDCA | Glucose | $CrCl_3$/Amberlyst-15, AuPd/HT | 95 | n/a ($O_2$) | n/a | n/a | 50 | 812 |

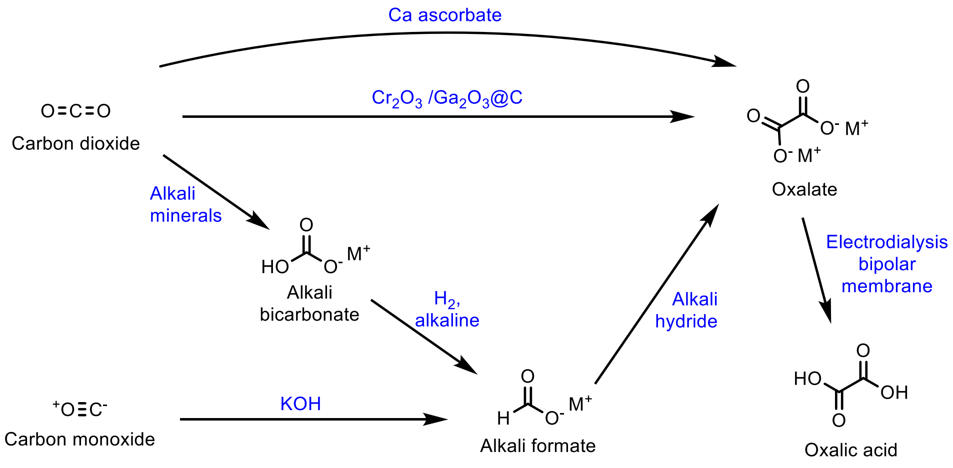


**Figure 67.** Selection of routes to OA from $CO_2$ and CO feedstocks, *via* electrochemical and chemical processes.

studied for OA production from $CO_2$, including Ag and Pd porphyrins, Rh-S clusters, and Ir, Co, Sa and Cu complexes.[745−749] In 2012, Kumar *et al.* utilized a Cu-based MOF and tetrabutylammonium tetrafluoroborate in DMF to give OA with 90%.[750] Sacrificial calcium ascorbate has been used as a non-toxic stoichiometric reducing agent for the conversion of $CO_2$ to OA, but the ascorbic acid precursor is more expensive than the OA product (Figure 67).[553]

Formate-to-oxalate coupling is one of the oldest routes to OA, and the development of formate production from $CO_2$ or CO places it as a pragmatic process for OA production.[728,751,752] Routes to formates include the hydrogenation of carbonates, photochemical reduction and caustic CO reduction.[728] Currently, alkali formates are commercially produced from CO and caustic alkalis, such as KOH (Figure 67).[753,754] Alternatively, $CO_2$ can be converted to bicarbonate *via* reaction with alkaline metals, and then hydrogenated to formate in an alkaline environment, with Ni-based catalysts found to be the most effective with 77% formate yield.[755] To avoid the need for external $H_2$ supply, processes utilizing reducing agent as hydride donors have been investigated.[756,757] In a 2016 patent, carbonate salts were converted to formate with yields as high as 99% at 90 °C, using sodium nitrate and Aeroxide P90 $TiO_2$ catalyst.[757] Photocatalytic reduction of $CO_2$ to formate has been developed, and presents an attractive route to harnessing solar radiation for the production of valuable chemicals.[728,758,759] However, current systems are not commercially competitive due to low catalyst stabilities and efficiencies, with a maximum achieved formate yield of 65% when derived from $CO_2$, expensive equipment and slow reactions.[759−762]

Formate coupling was found to occur when alkali metal formates are heated to 400 °C in the absence of air or oxygen, with oxalate obtained with a selectivity greater than 70%.[763] Sodium and potassium formate give high oxalate yields of 91 and 82%, respectively, *via* heating at 390 and 455 °C, respectively.[744,764] The oxalate yields from sodium and potassium formate were increased to 94 and 99%, respectively, using potassium hydroxide and alkali hydride as catalyst, respectively (Figure 67, Table 18, entry 7).[744] Potassium formate gave the highest oxalate yield at a much-reduced temperature of 200 °C, and the large catalytic effect highlights the possibility of further reductions in reaction temperature and time *via* the development of new catalyst types.[744] The conversion of the generated oxalate to OA can be accomplished simple with organic or inorganic acids, or *via* electrodialysis (Figure 67).[765−768] Electrodialysis bipolar membranes (EDBM), in particular, are effective for producing organic acids *via* water splitting in bipolar membranes. EDBMs are used in multiple industrial processes, including wastewater desalination and lithium battery recycling.[728] Processes that couple the electrodialysis process with other electrochemical processes are in development and could lead to additional production of high-value chemicals parallel to the salt splitting required to form OA.

*5.1.1.2. C3 Diacid.* Malonic acid (MalonA, 1,3-propanedioic acid) currently has little usage in polymer synthesis, but it could act as a feedstock to 1,3-propanediol synthesis, which in turn is a precursor to polytrimethylene terephthalate.[813] Very few studies have investigated the synthesis of MalonA from biomass sources, but an article by Yan *et al.* found that hydrothermal degradation of cellulose above 160 °C gave a

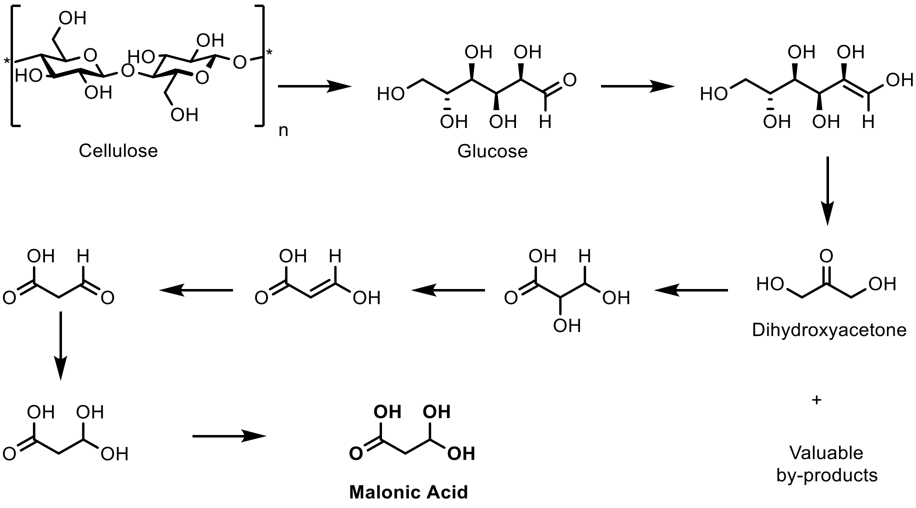


**Figure 68.** Pathway to malonic acid from cellulose *via* hydrothermal degradation.

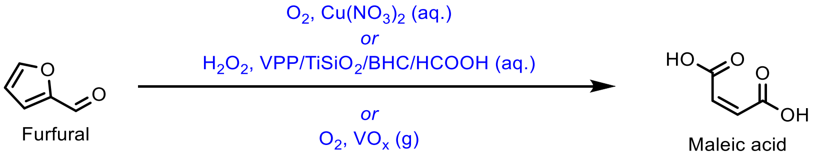


**Figure 69.** Summary of several reaction conditions for the oxidation of furfural to maleic acid. VPP = Vanadyl pyrophosphate, and BHC = betaine hydrochloride.

range of valuable products, one of which being MalonA (Figure 68).[769] Degradation of a homogenous cellulose solution yielded lactic, acetic and formic acid, and up to 40% MalonA (Table 18, entry 8). An alternative route from malic acid to the more-stable dimethyl malonate (67%) proceeds *via* esterification and oxidative decarboxylation (Table 18, entry 9).[770] Malic acid is considered a promising sugar-derived building block, although it is currently industrially produced *via* hydration of maleic anhydride (MalAn), which currently is limited in its synthesis from renewable feedstocks.[731]

*5.1.1.3. C4 Diacids.* Maleic acid (MalA, *cis*-butenedioic acid) is a chemical used in most fields of the chemical industry, in particular within unsaturated polyester resins.[772] Maleic anhydride (MalAn) is also widely used and the two chemicals can be readily interconverted by hydration or dehydration steps, such that the production of either chemical implies the availability of the other.[731] The most studied biomass feedstocks for conversion into MalA are furfural and 5-HMF, although 1-butanol and levulinic acid have also been investigated (Figure 65).[777,778,805,814,815]

Furfural is produced from waste agricultural carbohydrate feedstock on a scale of 250−400 kT annum$^{-1}$ and can be oxidized into MalA in either the liquid or the gas phase (Figure 69).[814,816] The gas phase oxidation of furfural to MalAn is currently performed with vanadium-oxide based catalysts at temperatures between 200 and 360 °C (Table 18, entry 10).[771] While the maximum yields reach 90%, the specific structures of the vanadium supports are critical to their catalytic activity. Additionally, furfural is prone to polymerization in $O_2$, hence deactivating the catalyst, although this can be minimized by using high temperatures and high $O_2$/furfural ratios.[817,818]

With $O_2$ as oxidant in the aqueous phase with $Cu(NO_3)_2$, Yin *et al.* reached 86% furfural conversion yet low MalA yield (i.e., 24%).[819] MalA yield was increased to 34.5% using a biphasic system, with a phosphomolybdic acid catalyst to suppress the furfural polymerization reaction, but tedious separation steps, made the system uncompetitive (Table 18, entry 11).[772] Ca-doped copper phosphate gave an increased productivity but a low MalA yield of 37% and suffered from significant catalyst deactivation.[814] Replacing $O_2$ with $H_2O_2$ is somewhat less desirable from a sustainability perspective, but enables the oxidation of furfural at milder conditions, although a high ratio of $H_2O_2$/furfural is required to ensure selective formation of MalA.[590,820] Metal-based and Brønsted-acid catalysts are used for furfural oxidation with $H_2O_2$, and the highest MalA productivity was observed with a heterogenous vanadyl pyrophosphate based catalyst and a low $H_2O_2$/ furfural ratio of 3, albeit with a low MalA yield of 36%.[821] Titanium silicalite zeolite catalysts produce MalA with a yield of 78% with a $H_2O_2$/furfural ratio of 7.5, but exhibit deactivation due to impurities in the corncob-derived furfural.[822−824] The deactivation can be alleviated with a $\gamma$-valerolactone (GVL)/$H_2O$ biphasic system, in which the MalA yield starts above 70% and levels off at 45%, even after 21 cycles (Table 18, entry 12).[773]

The deactivation of metal catalysts can be completely avoided using an organic acid, such as the sugar-beet-derived strong acid betaine hydrochloride (BHC).[731] In aqueous solution, with a $H_2O_2$/furfural ratio of 10, BHC afforded a 61% yield of MalA, as well as a 31% yield of fumaric acid (Table 18, entry 13).[774] Unlike other strong acids such as HCl, BHC can be recovered and reused without performance degradation. Formic acid can be used as both the solvent and catalyst, yielding 91% MalA with a $H_2O_2$/furfural ratio of 3, although the productivity of the system was low due to peracid formation reducing the solution acidity (Table 18, entry 14).[775,825] The MalA yield was found to decrease with increasing number of carbons of organic acid used, with butyric acid only yielding 37% MalA.[775]

5-HMF is also reported as a starting material for the liquid-phase conversion to MalA, making use of a heterogeneous vanadium-based catalyst in GVL, due to detrimental effects seen with protic solvents such as water.[815] The highest MalA selectivity reported (85% at 36% 5-HMF conversion) utilized $Fe_3O_4@SiO_2$ as catalyst (Table 18, entry 15).[776] The aforementioned formic acid procedure, repeated with 5-HMF, gave the best overall results, with 89% yield of MalA and a productivity more than twice that of the previous method (Table 18, entry 16).[775] The gas-phase conversions of 1-butanol and levulinic acid (LevA) to MalAn have also been reported.[777,778] Cavani *et al.* used vanadyl pyrophosphate to produce MalAn with a 39% yield from 1-butanol in air, but the system productivity was low and high purity 1-butanol was required (Table 18, entry 17).[777] Improvements in feedstock purity and robust catalysts are desirable to expand the potential of the oxidation reaction. A $VO_x/SiO_2$ catalyst yielded MalAn with a yield of 71% from LevA, although the low melting point, high viscosity and low thermal stability of LevA are potential barriers to continuous industrial production (Table 18, entry 18).[778]

Fumaric acid (FA, *trans*-butanedioic acid) is used in the food industry, for feed processing and in the synthesis of unsaturated polyesters.[826] The current methods for FA synthesis are primarily isomerization from MA and fermentation, although there are few relevant studies.[774,827] During the conversion of furfural to MA, FA is produced as a side-product resulting from the MA double bond *cis-trans* isomerization (Figure 70).[774] Current industrial production uses a homogeneous thiourea catalyst, but a poly(4-vinylpyridine) resin has been presented as a heterologous alternative (Table 18, entry 20).[827] FA yields of 78% from MA have been obtained, but decreased significantly when initial concentrations of MA above 0.02 wt % were used, and catalyst deactivation was quickly observed. Without catalyst, the reaction proceeds readily at 200 °C, but this causes a color change, which can be considered disadvantageous for some applications (Table 18, entry 19).[779]

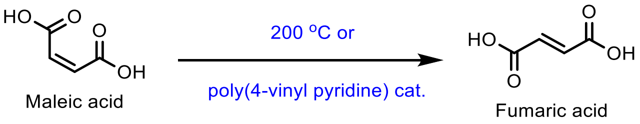


**Figure 70.** Isomerization of maleic acid to fumaric acid, at elevated temperatures, with a thiourea catalyst or with a poly(4-vinylpyridine) catalyst.

Succinic acid (SA, 1,4-butanedioic acid) is widely used in the food, chemical and pharmaceutical industries. Additionally, it is an important monomer for the preparation of biodegradable polymers, such as polybutylene succinate.[828−830] SA is produced predominantly *via* the hydrogenation of petrochemically derived maleic anhydride, but is also commercially produced from biomass *via* a fermentative process, albeit generating significant $Ca_2SO_4$ waste during purification and thus decreasing SA productivity.[831,832] Hence, it is worthwhile exploring recent developments in the synthesis of SA from biomass, *via* both biotechnological and catalytic routes.

An excellent review by Li *et al.* has recently discussed advances in biotechnological routes to prepare SA from renewable feedstocks.[833] Typically, yeasts are more well-suited to fermentative SA production due to their abilities to use alternative feedstocks in a variety of adverse conditions. Current commercial routes typically use *E. coli* and glucose feedstocks. With an engineered *Y. lipolytica* strain, the highest-obtained SA titer, i.e., 209.7 g $L^{-1}$, was achieved from a crude glycerol feedstock, with a yield of 0.45 g $g^{-1}$ (Table 19, entry 1).[834−836] *Y. lipolytica* has been used to obtain a lower but nevertheless significant titer of 33.2 g $L^{-1}$ SA from glucose, and can also utilize a range of additional feedstocks for SA production, including ethanol, rapeseed oil and even *n*-alkanes (Table 20, entry 2).[837−840] The metabolic engineering employs strategies such as the blocking of a step within the TCA cycle, preventing the desired product from being further converted in the metabolic cycle (Figure 71).

**Table 19. Microorganisms, Conditions and Yields for the Chemical Production of Selected Products from Biomass Sources *via* Biotechnological Conversion**

| Entry | Class | Product | Feedstock | Microorganism | Titer (g $L^{-1}$) | Yield (mol %) | Mass yield (g $g^{-1}_{\text{feedstock}}$) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1 | Diacid | Succinic acid | Glycerol | *Y. lipolytica* | 210 | 71 | 0.45 | 834 |
| 2 | Diacid | Succinic acid | Glucose/Xylose | *Y. lipolytica* | 33 | n/a | 0.58 | 837 |
| 3 | Diacid | Adipic acid | Glucose | *T. fusca* | 2.2 | n/a | 0.045 | 850 |
| 4 | Diacid | Adipic acid | Glycerol | *E. coli* | 68 | 73 | 0.38 | 851 |
| 5 | Diacid | Adipic acid | Fatty acids | *C. tropicalis* | 50 | n/a | n/a | 547 |
| 6 | Diol | Ethylene glycol | Xylose | *E. coli* | 108 | 87 | 0.36 | 852 |
| 7 | Diol | Ethylene glycol | Xylose | *E. coli* | 40 | 85 | 0.35 | 853 |
| 8 | Diol | 1,3-PDO | Glycerol | *K. oxytoca* | 76 | n/a | n/a | 854 |
| 9 | Diol | 1,3-PDO | Glucose | *E. coli* | 135 | n/a | n/a | 855 |
| 10 | Diol | 1,4-BDO | Glucose | *E. coli* | 120 | 80 | 0.40 | 597 |
| 11 | Diol | 1,4-BDO | Xylose | *E. coli* | 12 | 43 | 0.37 | 856 |
| 12 | Diol | 2,3-BDO | Glucose | *K. pneumoniae* | 150 | n/a | n/a | 857 |
| 13 | Diol | 1,3-BDO | Glucose | *E. coli* | 13 | 0.57 | 0.29 | 858 |
| 14 | Diamine | 1,3-PDA | L-Aspartate | *E. coli* | 13 | n/a | 0.1 | 859 |
| 15 | Diamine | 1,4-BDA | Glucose | *E. coli* | 42 | n/a | 0.26 | 860 |
| 16 | Diamine | 1,5-PeDA | L-Lysine | *E. coli* | 221 | 92 | 47 | 861 |
| 17 | Diamine | 1,5-PeDA | Glucose | *C. glutamicum* | 104 | 54 | 30 | 862 |
| 18 | Diamine | 1,5-PeDA | Xylose | *C. glutamicum* | 103 | 32 | 22 | 863 |

Table 20. Catalysts, Conditions and Yields for the Production of Selected Diols from Biomass Sources *via* Chemical Conversion

| Entry | Diol | Feedstock | Catalyst | Temperature (°C) | Pressure (bar) | Conversion (%) | Selectivity (%) | Yield[a] (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | EG | Cellulose | Al-$WO_3$-Ni-TUD-1 | 230 | 40 ($H_2$) | 100 | 76 | 76 | 1044 |
| 2 | EG | Cellulose | Ni-W/SBA-15 | 245 | 60 ($H_2$) | 100 | 76 | 76 | 1045 |
| 3 | EG | Cellulose | Ru/$WO_3$ | 240 | 40 ($H_2$) | 100 | 76 | 76 | 1046 |
| 4 | EG | Pre-treated lignocell. | Ni-W/MCM-41 | 250 | 60 ($H_2$) | n/a | n/a | 64 | 1018 |
| 5 | EG | Pre-treated lignocell. | Ru/C + m-$WO_3$ | 245 | 60 ($H_2$) | 100 | 63 | 63 | 1019 |
| 6 | EG | Pre-treated lignocell. | RANEY Ni + SPT | 245 | 60 ($H_2$) | n/a | n/a | 35 | 1020 |
| 7 | EG | Glucose | Ni-$W_2C$/AC | 245 | 60 ($H_2$) | n/a | n/a | 35 | 1023 |
| 8 | EG | Glucose | Ni-$W_2C$/AC | 245 | 60 ($H_2$) | 100 | 47 | 47 | 1023 |
| 9 | EG | Glucose | Ru/AC + AMT | 240 | 50 ($H_2$) | n/a | n/a | 60 | 1024 |
| 10 | EG | Lignocell. hydrolysate | RANEY Ni + NaOH | 230 | 110 ($H_2$) | n/a | n/a | 19 | 1025 |
| 11 | EG | Glycerol | Cu/ZnO/$MO_x$ | 300 | 1 ($H_2$) | 100 | 37 | 37 | 1028 |
| 12 | EG | Glucose | 1) n/a<br>2) n/a<br>3) Ru/C | 1) 527<br>2) 230<br>3) 80 | 1) n/a<br>2) Cu/C<br>3) 90 ($H_2$) | n/a | n/a | 98 | 1036 |
| 13 | 1,2-PDO | Glycerol | Ru-Cu/modified bentonite | 230 | 80 ($H_2$) | 100 | 85 | 85 | 1029 |
| 14 | 1,2-PDO | Glucose | 1) $Ca(OH)_2$ + CuCr<br>2) $Ca(OH)_2$ + CuCr | 1) 140<br>2) 220 | 1) 60 ($H_2$)<br>2) 60 ($H_2$) | 100 | 53 | 53 | 1047 |
| 15 | 1,2-PDO | Cellulose | $Ca(OH)_2$ + CuCr | 245 | 60 ($H_2$) | 100 | 43 | 43 | 1048 |
| 16 | 1,2-PDO | Lignocellulose | Ni-$W_2C$/AC | 245 | 60 ($H_2$) | n/a | n/a | 39 | 1049 |
| 17 | 1,2-PDO | Lignocell. Hydrolysates | RANEY Ni + NaOH | 230 | 110 ($H_2$) | n/a | n/a | 41[b] | 1025 |
| 18 | 1,3-PDO | Glycerol | Pt/$WO_x$/AlOOH | 180 | 50 ($H_2$) | 100 | 66 | 66 | 1050 |
| 19 | 1,3-PDO | Glycerol | Pt-Cu/Zeolite | 210 | 1 ($H_2$) | 90 | 59 | 53 | 1051 |
| 20 | 1,4-BDO | Dimethyl maleate | Cu/SBA-H | 220 | 50 ($H_2$) | 100 | 66 | 66 | 1052 |
| 21 | 1,4-BDO | SA | Re-Pd/C | 160 | 150 ($H_2$) | 100 | 66 | 66 | 1053 |
| 22 | 1,4-BDO | Furfural | Pt/$TiO_2$-$ZrO_2$ | 120 | 35 ($H_2$) | 1) 96<br>2) 97 | 1) 94<br>2) 98 | 85 | 1054 |
| 23 | 1,5-PeDO | Furfural | 1) Ni<br>2) $\gamma$-$Al_2O_3$<br>3) nr<br>4) 45 ($H_2$) | 1) n/a<br>2) 375<br>3) 130<br>4) Ru-$TiO_2$ | 1) n/a<br>2)) n/a<br>3) 17 (He)<br>4) 120 | n/a | n/a | 80 | 1055 |
| 24 | 1,6-HDO | HMF | Pd/$SiO_2$ + Ir-$ReO_2$/$SiO_2$ | 100 | 70 ($H_2$) | 100 | 58 | 58 | 1056 |
| 25 | 1,6-HDO | THFDM | Pt$WO_x$/ $TiO_2$ | 160 | 55 ($H_2$) | n/a | n/a | 83 | 1057 |
| 26 | 1,6-HDO | Cellulose | 1) $H_2SO_4$<br>2) Ni/$SiO_2$<br>3) Pd/$SiO_2$-$Al_2O_3$ | 1) 210<br>2) 150<br>3) 160 | 1) 69 (He)<br>2) 34.5 ($H_2$)<br>3) 55 ($H_2$) | n/a | n/a | 27 | 1055 |

[a]Molar yield of target diol. [b]Mass yield of target diol.

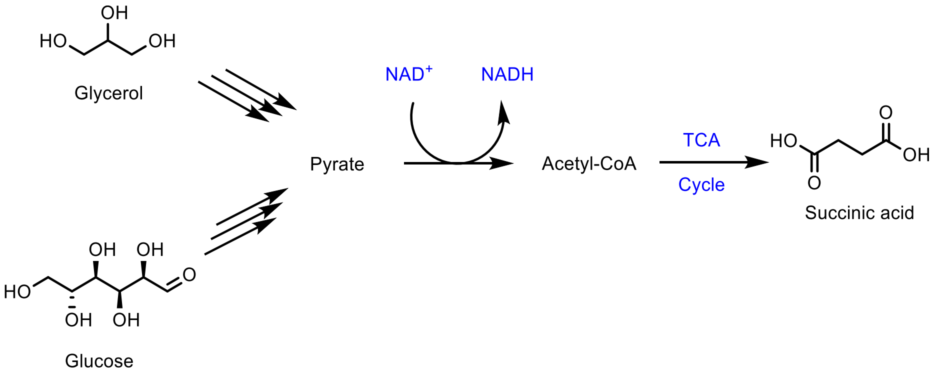


**Figure 71.** Biotechnological production of succinic acid from feedstocks including glucose and glycerol, *via* deletion of a succinate-metabolizing gene in the tricarboxylic acid (TCA) cycle.

Chemically, xylose can be converted into SA using Brønsted acid catalysts directly or indirectly *via* furfural (Figure 72).[590,820,841,842] Indirectly, xylose can be converted to furfural using Brønsted acids, either supported on metal−organic frameworks (MOFs) or complimented by Lewis acids such as $CrCl_3$, with SA yields exceeding 70%.[842,843] Conversion of furfural to SA with the Brønsted acid Amberylst-15 resin in aqueous $H_2O_2$ gave a 74% SA yield at full conversion,

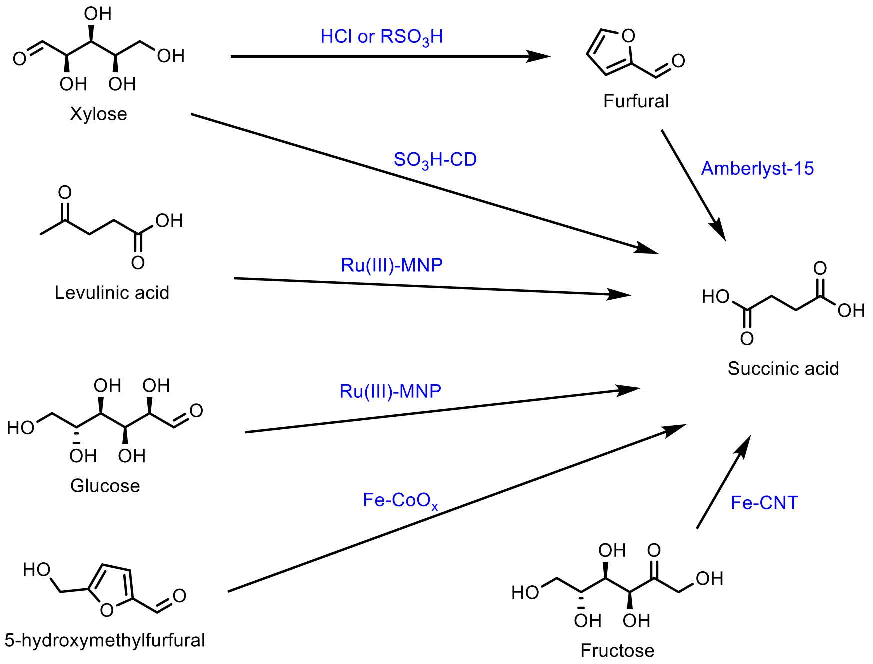


**Figure 72.** Chemical routes to succinic acid from a range of biomass sources.

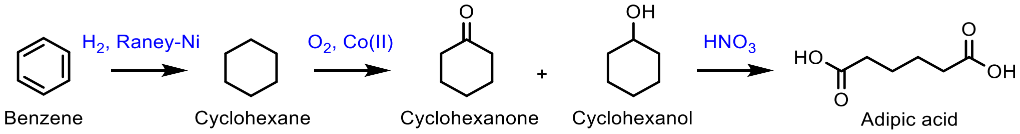


**Figure 73.** Dominant petrochemical route to adipic acid *via* the nitric acid oxidation process.

attributed to the interactions of the Amberlyst-15 aromatic ring with the furfural furan ring.[590,820,844] Direct conversion of xylose to SA resulted in numerous side-reactions, including furfural polymerization, unless a toluene/$H_2O$ biphasic system was used, in which case a 52% SA yield.[841] A $SO_3H$-CD-carbon catalyst with ultrasound irradiation increased the SA yield to 81% due to the increased interfacial area and increased mass and heat transfer (Table 18, entry 21).[780] SA yields of up to 93% were obtained using a N-doped $SO_3H$-carbocatalyst, although this catalyst suffered serious deactivation due to acid site leaching.[845]

The conventional process to SA from LevA utilizes hazardous nitric acid or mercury.[846,847] A yield of 78% SA was obtained from LevA using 4 wt % ruthenium on silica magnetic nanoparticles ($Ru^{III}$-MNP) in the presence of $H_2O_2$, which were easily separated using magnetism and reused with negligible Ru leaching, and further investigation with concentrated LevA and lower catalyst loading would be useful to evaluate the industrial potential of this route (Figure 72, Table 18, entry 22).[781] To avoid metal-leaching, trifluoroacetic acid was used to convert LevA into SA in the presence of $H_2O_2$, yielding 60% SA after separation (Table 18, entry 23).[782] The employed acid could potentially be recycled *via* dehydrating the azeotrope.[848,849]

Glucose was converted to SA with the aforementioned $Ru^{III}$-MNP catalyst, achieving SA yields of 62% at full conversion (Figure 72).[864] A SA selectivity of 88% could be maintained after multiple runs *via* the continuous addition of *n*-butylamine. Ru-oxyhydride nanoparticles on N-doped graphene under similar conditions gave 87% SA from glucose, but with a low productivity (Table 18, entry 24).[783] A high SA selectivity of 81% was achieved from 5-HMF at 90% conversion in the presence of NaOH using a silica-immobilized Fe/Co-oxide based catalyst (Figure 72, Table 18, entry 25).[776] Changing the base to *n*-butylamine increased the conversion but decreased the productivity, which was proportional to the basicity of the reaction medium. Dibendetto and co-workers used Fe-CNT catalysts for the production of OA from fructose, with SA produced as a side-product (Figure 72, Table 18, entry 26).[738] Although initially high, the SA selectivity dropped to 21% by the time 99% fructose conversion was reached. Of the available feedstocks, monosaccharides such as glucose and fructose are among the most cost effective, but improvements to the reported catalysts are required before commercial-scale production could become viable.[731]

*5.1.1.4. C6 Diacid.* Adipic acid (AA, 1,6-hexanedioic acid) is produced on a scale of >3 MT annum$^{-1}$, primarily for use in nylon 66, the most commonly used polyamide.[865] Currently, adipic acid is mainly made *via* the nitric acid oxidation process.[865,866] In this process, petrochemical benzene is reduced to cyclohexane, converted over a Co(II) catalyst to a mixture of cyclohexanone and cyclohexanol, called KA oil, and eventually oxidized to adipic acid with nitric acid (Figure 73).[866] During the conversion, 90% of the unreacted cyclohexane must be recycled to prevent over-oxidation. A similar route utilizing cyclohexene is also used, although nitric acid is still required, generating potent $NO_x$ greenhouse gases.[867,868] Currently, $NO_x$ released from AA production constitutes 20% of the $CO_2$-equivalent emissions of the entire petrochemical production industry, as the warming potential of $NO_x$ is ∼300 times greater than $CO_2$.[869−871] Despite technologies to reduce $NO_x$ emissions, such as flue gas

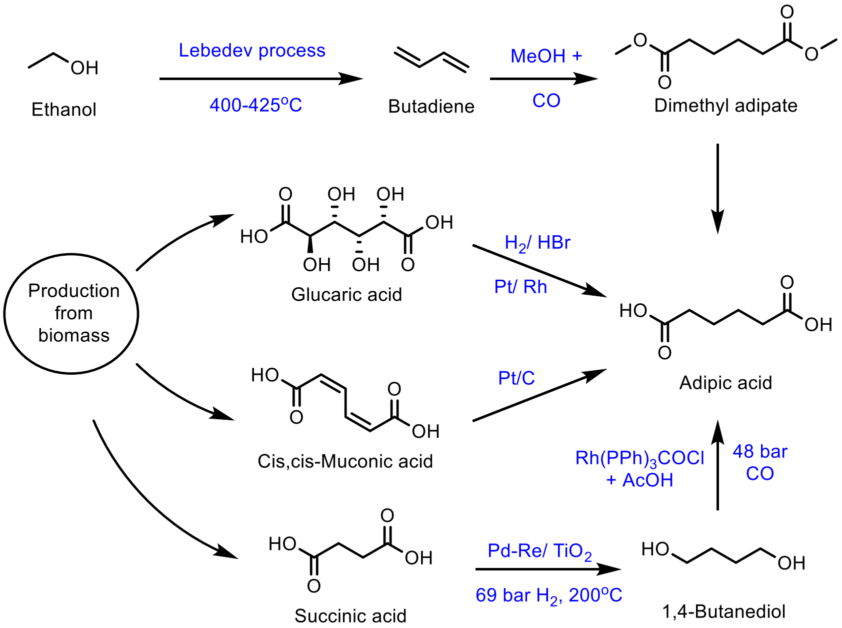


**Figure 74.** Methods for bio-based adipic acid production from ethanol, glucaric acid, *cis,cis*-muconic acid and succinic acid *via* chemical conversions.

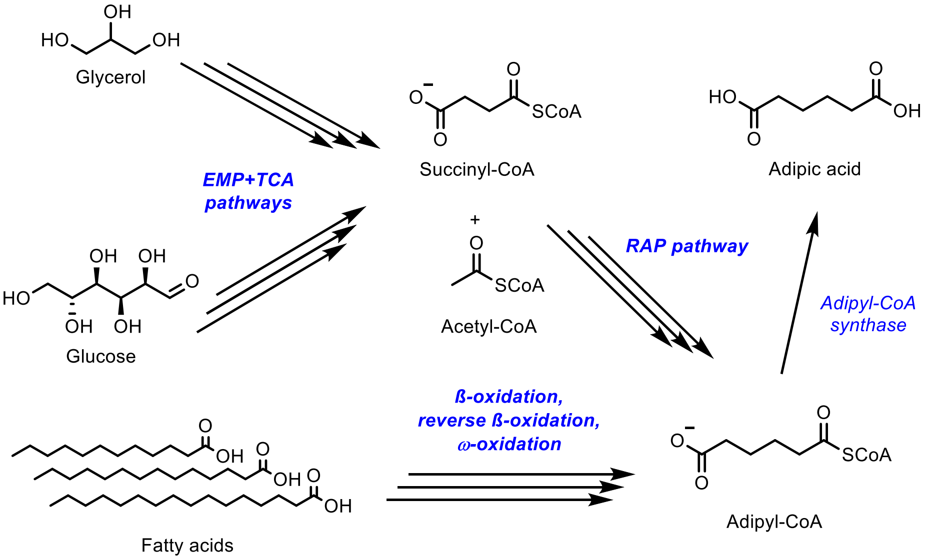


**Figure 75.** Direct biotechnological routes to adipic acid from glycerol, glucose and fatty acids, with the multiple steps of the tricarboxylic acid cycle (TCA), the glycolysis pathway (EMP), the reverse adipate pathway (RAP), the $\beta$-oxidation cycle, the reverse $\beta$-oxidation cycle and the $\omega$-oxidation cycles simplified into single steps.

recirculation, many plants operate without recycling policies in place.[872−875] Despite being extremely inefficient, the NO process will remain the major route until more-sustainable routes can be scaled at a similar cost.[865,872,876]

One route to $NO_x$ free AA production is using alternative oxidants, such as $H_2O_2$ and $O_2$.[872,876−878] Several studies show high yields of AA obtained from cyclohexene with $H_2O_2$, on a large scale,[872,877,879−883] as well as from cyclohexanone in water with ferrous catalyst and $H_2O_2$.[884] However, life cycle analysis of $H_2O_2$ raises even greater concerns than NO, due to the rather polluting "anthraquinone process" used for its production.[865,880,885] Air and $O_2$ are also used widely as alternative oxidants.[865] A commercialized route utilizes air for the conversion of cyclohexane to cyclohexanol/cyclohexanone, which is then combined with acetic acid to give AA with a yield of 50−70%, albeit with significant side products.[872,886−888] However, the high required AA purity means the acetic acid must be completely removed.[787,872] Currently, air/$O_2$ oxidation routes are uncompetitive due to a lack of adequate catalysts.[865]

An alternative route to $NO_x$ free AA is to change the feedstock. Several substrates have been explored, including phenol, butadiene, adiponitrile and cyclohexene.[872,876,886] However, these are still derived from benzene, and the phenol-based processes still generates $NO_x$.[872,889] Butadiene is the most promising alternative, which can be converted with MeOH and CO (syngas) to dimethyl adipate with yields as high as 96%, and subsequently converted to adipic acid without producing $NO_x$ (Figure 74, Table 18, entry 27).[784,890,891] Assuming some optimizations, this process

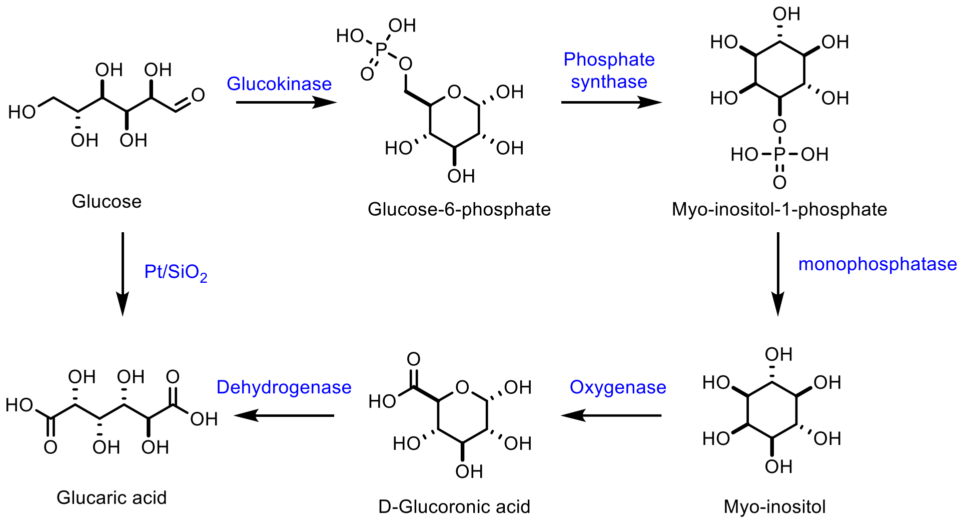


**Figure 76.** Chemical and biotechnological routes from glucose to glucaric acid.

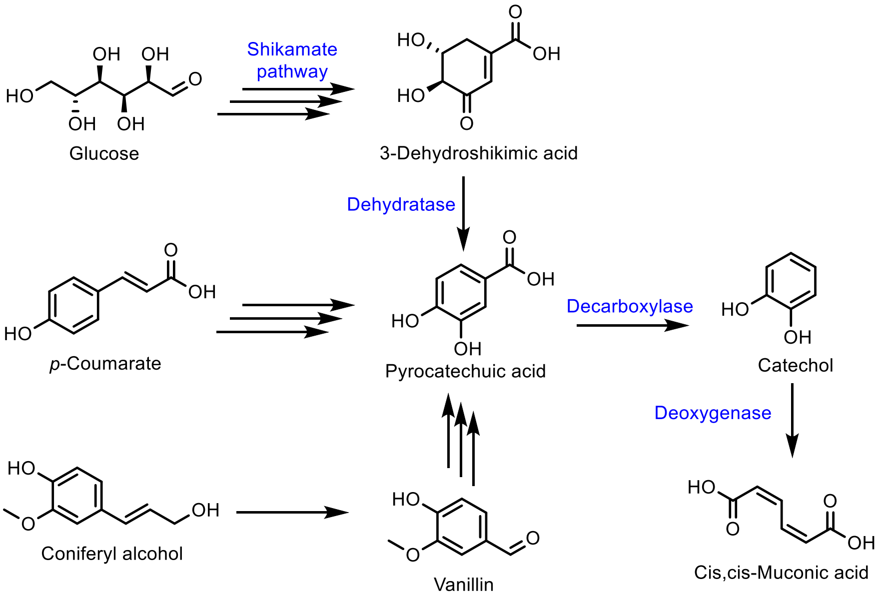


**Figure 77.** Biotechnological routes to *cis,cis*-muconic acid from glucose and lignin-derived aromatic compounds such as *p*-coumarate, coniferyl alcohol and vanillin.

could potentially compete with the NO process, but an unstable butadiene price has prevented adoption of this technology.[865] Butadiene can be produced from sustainable biomass *via* several routes, the most prominent of which is the direct conversion from bio-sourced ethanol.[665,892,893] Bio-ethanol derived butadiene would be 13−26% more expensive than conventional butadiene, but this difference would likely decrease as the catalysts are improved and the petrochemical feedstocks become less abundant. While the bioethanol route to butadiene avoids petrochemical consumption and results in significant reductions in $CO_2$ emissions, the energy demand and water consumption of the route are substantially higher, increased by factors of ∼100 and ∼2, respectively.[892]

Enzymatic routes and combinations of enzymatic and conventional chemical routes provide additional pathways to bio-based AA. AA only appears as a metabolic intermediate at trace levels, so other routes have been explored.[850,894−898] The reverse adipate pathways could theoretically produce AA from glucose with molar yields as high as 92%, although only a titer of 2.2 g $L^{-1}$ has been obtained from glucose with an engineered *Thermobifida fusca* strain (Figure 75, Table 19, entry 3).[850,889,899,900] Significantly higher yields have been achieved using glycerol, with an engineered strain of *E. coli* giving a titer of 68 g $L^{-1}$ AA with a yield of 0.34 g $g^{-1}$ (Figure 75, Table 19, entry 4).[900]

Oxidative pathways containing a mixture of $\beta$-oxidation, reverse $\beta$-oxidation and $\omega$-oxidation processes enable the production of AA from a range of renewable substrates, including glycerol, glucose and fatty acids (Figure 75).[865,889,894,901,902] While *E. coli.* has only yielded AA titers below 1 g $L^{-1}$ from glycerol, significantly higher titers have been obtained from engineered yeasts.[865,901] By disrupting the enzymes responsible for degrading C6 acyl chains, fatty acids are degraded to adipic acid but no further. Using this method, Picataggio and coworkers modified *C. tropicalis* to yield ∼50 g $L^{-1}$ AA from coconut oil. This has been scaled to 300 L, although this commercial effort was halted in 2018 (Table 19, entry 5).[547,903−907] Neither glycerol nor vegetable oil sources are economically competitive with NO, as waste glycerol is unsuitable for the process due to impurities and insufficient supply.[865] Additional pathways such as the 2-oxopimelic acid pathway, the polyketide synthase pathway, and the lysine conversion pathways have been proposed, with only the first two demonstrated, both of which gave titers of <0.5 g $L^{-1}$.[889,898,908]

Several indirect routes combining the production of an intermediate *via* chemical or fermentative processes with the biotechnological conversion to AA have been developed. The most-studied intermediates are succinic acid (SA), glucaric acid (GA) and *cis,cis*-muconic acid (MucA), with their conversions to AA shown in Figure 74.[865,889,894,896,902,909] All three intermediates are naturally occurring and have additional potential as platform chemicals outside of AA synthesis.[895,910−914] The first important intermediate, SA, can be converted to AA *via* hydrogenation to 1,4-butanediol followed by catalytic carboxylation, with the second step yielding 74% AA using a $Rh(PPh)_3COCl$ catalyst (Table 18, entry 28).[785,915] Although scaled up to a pilot-plant, the process has not yet been commercialized due to the energy intensive conversion.[865] Other biotechnological routes directly to 1,4-butanediol from sugars have been developed, which could be combined with the aforementioned routes to produce AA.[916]

The second important intermediate, GA, is a C6 dicarboxylic acid with a hydroxy group on each of its 4 internal carbons and has uses within the biomedical industry and within polymer chemistry.[910,914,917] A 3-step pathway from glucose to GA has been developed, and *Saccharomyces cerevisiae* was used to give a titer of 6 g $L^{-1}$ GA after 200 h (Figure 76).[910,918−921] A slight improvement to 6.6 g $L^{-1}$ GA after 80 h was obtained through co-feeding an engineered *Pichia pastoris* strain glucose and myo-inositol.[922] A 2-step chemo-catalytic route from glucose to AA, *via* GA, has also been developed (Figure 76), with the second step applicable to GA obtained from enzymatic pathways.[896] The oxidation and subsequent hydrodeoxygenation process has been piloted with AA yields of up to 89%, although significant amounts of base are required for the glucose oxidation, and improved catalyst longevity is desirable (Table 18, entry 29).[260,786,865,896,923−925]

The third important intermediate (MucA) is a natural intermediate produced in several microbes, and can be converted to AA *via* hydrogenation using various catalysts such as Pt/C, with yields up to 97% (Figure 77, Table 18, entry 30).[787,889,926−928] MucA can also be isomerized to give *cis,trans*- and *trans,trans*-muconic acid, which have applications as a precursor for the synthesis of terephthalic acid and ε-caprolactam.[787,889,894,896,913] The shikimate pathway has been engineered and optimized for MucA production from glucose, with the highest production of 59.2 g $L^{-1}$ MucA observed by Frost *et al*. in an engineered strain of *E. coli*, with a molar yield of 30%.[889,909,913,926,929−932] Lignin-derived aromatic compounds such as *p*-coumarate, ferulate and benzoate have been utilized for biotechnological MucA production with glucose as a co-substrate in *P. putida*, with MucA titers reaching 50 g $L^{-1}$, beyond which the MucA toxicity becomes lethal.[911,933] To overcome the issue of toxicity limiting product titers, expression of these pathways in a more tolerant organism, i.e., *S. cerevisiae*, has been engineered, albeit only with low titers (140 mg $L^{-1}$).[931] An Iron(III) catalyst was used for the chemical conversion of lignin-derived catechol into MucA using benign oxidants, but the reaction rate was low.[934] Alternatively, an organic salt catalyst with $H_2O_2$ as an oxidant was used to give yields of up to 84%.[935] Recently, also the enzymatic reduction of MucA to AA has been described, and combining both the synthesis of MucA and subsequent conversion to AA would enable the direct conversion of renewable feedstocks to AA *via* MucA in a single microorganism.[936,937]

The purity demands for AA are high, and currently no method can competently remove acidic and other organic impurities to below the 20 ppm threshold required for use within nylon synthesis.[865] Attempted methods include utilizing the solubility of MucA in ethanol, reactive extraction and the utilization of deep eutectic solvents for extraction, but the purest MucA still contains 90 ppm of an elemental nitrogen impurity.[787,938−941] Purification is a massive hurdle for widespread adoption and more advanced routes from diverse bio-feedstocks will face even greater impurities that require removal.[865] This issue is not unique to bio-based feedstocks, as alternative petrochemical routes to AA have also been hindered by the purity requirement.[942] The three most promising routes to bio-based AA are the chemical conversion of butadiene, the chemical oxidation of glucose *via* GA, and the biotechnological reverse adipate pathway.[889] All three routes have potential for commercialization in the near future. Additionally, economic analysis of the biotechnological pathway *via* MucA suggested a roughly 2-fold cost reduction relative to the NO process, if lignin is used as a feedstock.[889] This is due to an extremely cheap estimation of lignin, as low as \$0.04 $kg^{-1}$, which would require significant additional progress in the area of lignin purification and valorisation.[943,944] As such, this route is still in its infancy, but arguably presents the best-case-scenario in the long term for AA synthesis.

#### 5.1.1.5. Long-Chain Diacids.

Several long-chain diacids have been produced both chemically and biotechnologically, although these are typically produced and utilized on scales much smaller than shorter chain diacids. In step-growth polymerization, utilizing longer monomers can increase chemical resistance due to a subsequent decrease in the concentration of vulnerable bonds such as esters and amides. Additionally, these monomers enable greater variation in the thermal and mechanical properties of polymers produced, although these also greatly depend on the nature of the polymer chains.

Pimelic acid (PimA, 1,7-heptanedioic acid) is commercially produced *via* the oxidation of cycloheptanone with dinitrogen tetroxide and a number of patents exist relating to the its production *via* various routes.[945−947] PimA was first identified as a metabolic intermediate in bacterial and yeast growth in 1964, and in 2011 Zhang *et al.* achieved a pimelic acid titer of 2.36 mg $L^{-1}$ using an engineered bacterial strain.[948] This exceptionally low titer highlights the lack of development in this area.

Suberic acid (SubA, 1,8-octanedioic acid) production from bio-based sources has not been the subject of many studies, although recently SubA has been produced with a yield of 13% from hydroxy cyclooctane *via* an enzymatic process using *E. coli*.[949] A 2014 patent for the production of SubA from γ-valerolactone and an alcohol follows a 4-step procedure.[950] Due to low monomer availability, SubA has not seen many applications within polymer chemistry, but the development of an efficient route to SubA from biomass sources could enable a range of novel polymers with interesting properties.

Azelaic acid (AzA, 1,9-nonanedioic acid) is produced from oleic acid, an unsaturated 18C fatty acid, *via* oxidative cleavage of the double bond. Oxidative cleavage is predominantly conducted *via* ozonolysis, which presents concerns regarding flammability and toxicity.[951] Hydrogen peroxide present a valid alternative, due to high atom economy and reduced safety concerns compared to gaseous reactants.[952−956] The process can either proceed in two steps or, more recently, in a single step, although the latter can require high catalyst loadings.[954−957] Benessere *et al.* reported a method for both a two-step and a single-step process.[957] In the two-step process, tungstic acid and $H_2O_2$ at 343 K convert oleic acid to a 9,10-dihydroxystearic acid intermediate, which was then fully converted to AzA by NaOCl at 25 °C with a maximum overall yield of 54%. In the one-step process, tungstic acid and $H_2O_2$ alone gave a high AzA yield of 91%, albeit with an increased ratio of $H_2O_2$ to oleic acid, increased reaction temperature (i.e., 373 K) and extended reaction time (i.e., 8 h).

Sebacic acid (SebA, 1,10-decanedioic acid) is mainly produced industrially *via* alkali saponification or catalytic hydrolysis of castor oil to ricinoleic acid, and subsequent alkali cracking, acidification, and purification.[958] Biotechnological routes to SebA have been investigated for production from bio-based sources with reasonably productive results, as is discussed in a recent review by Li *et al.*[959] An engineered strain of *E. coli* has been used to convert natural fats to SebA with yields reaching 50−60%.[960] Suigharto *et al.* utilized the biotechnological transformation of methyl decanoate to produce SebA with a yield of 27 g $mol^{-1}$ and a productivity of 0.5 g $L^{-1}$ $h^{-1}$.[961] From glycerol, a readily available sustainable feedstock, a 0.06 g $L^{-1}$ titer of SebA has been achieved, *via* $\beta$- and $\omega$-oxidation.[901,962] An engineered *C. tropicalis* was used to convert decane into SebA with a titer of 0.94 g $L^{-1}$ $h^{-1}$, which has potential for future sustainability due to the possibility of alkane production by enzymatic processes.[963,964]

Longer chain $\alpha,\omega$-diacids can be produced catalytically *via* the metathesis of unsaturated fatty acids or biotechnologically *via* conversion of various renewable feedstocks.[965,966] The self-catalysis of a number of unsaturated fatty acid and their ester derivatives with Ru-based Grubbs catalysts yielded a series of straight chain C18−C26 $\alpha,\omega$-dicarboxylic acids and esters, with yields ranging from 39% to 82%.[966] However, these reactions suffer from harsh conditions, multi-step processes, and costly separations. Lee *et al.* reviewed the current state of long-chain diacid production from vegetable-oil sources *via* enzymatic processes, which avoids several of the aforementioned metathesis issues.[965] Alkanes are currently the most effective substrate for conversion to long-chain $\alpha,\omega$-diacids *via* $\alpha,\omega$-oxidation, although their current petrochemical source limits their potential as a sustainable feedstock.[963,965] Fatty acids can be converted into $\alpha,\omega$-diacids *via* three metabolic processes, where the $\omega$-carbon is sequentially oxidized to form a $\omega$-hydroxy fatty acid, a $\omega$-oxo-fatty acid and finally an $\alpha,\omega$-diacid.[965] The suppression of $\beta$-oxidation pathways and the overexpression of $\omega$-oxidation pathways are identified as strategies for increased $\alpha,\omega$-diacid productions.[965] Croda has patented the production of a C36 diacid obtained from the dimerization of unsaturated oleic and/or linoleic acids *via* Diels−Alder coupling, or a similar process (Figure 78).[967] The non-terminal nature of the unsaturation in these fatty acids gives two alkyl branches. Whereas straight-chain long-chain aliphatic diacids are typically solids that increase the melting and glass transition points of polymers they are incorporated in, the C36 diacid is a liquid at room temperature, and reduces the glass transition and melting points of polymers, due to the long alkyl branches interrupting the polymer chain packing.

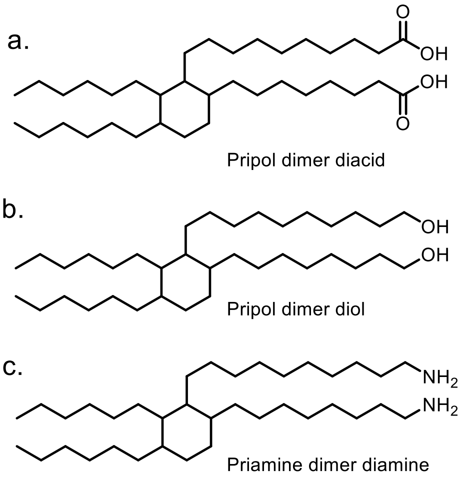


**Figure 78.** Long-chain C36 diacid, diol and diamines commercialized by Croda (approximate structures with omitted double bonds along the chains).

*5.1.1.6. Aromatic Diacids.* Terephthalic acid (TPA) is produced on a massive scale exceeding 80 MT annually, primarily for the production of polyethylene terephthalate (PET) and some other polyesters.[968] Currently, the vast majority of TPA is produced *via* the oxidation of *p*-xylene, which is obtained *via* catalytic reforming of petrochemical naphtha (Figure 79). The reforming process gives a mixture of aromatic compounds called BTX, largely consisting of benzene, toluene and xylene isomers.[731] Producing TPA from bio-based sources either involves the production of bio-based *p*-xylene for conventional conversion to TPA, or direct production of TPA from bio-based sources.

Several possible bio-based routes to *p*-xylene have emerged from feedstocks including furan, 2-methylfuran, ethylene, *iso*-butanol, 2,5-dimethanylfuran and HMF, as shown in Figure 80.[731] Catalytic fast pyrolysis (CFP) is a process that produces BTX from solid raw biomass with an inexpensive zeolite catalyst *via* Diels−Alder reactions with alkenes.[969−971] Following the fine-tuning of the pore structure of a coked ZSM-catalyst, the total *p*-xylene selectivity of the CFP of furan and 2MF with propylene reached 1.8 and 15%, respectively.[971−973]

Ethylene, which is commercially derived from sugarcane and corn (section 2.1), can be converted to *p*-xylene *via* a four-step process (Figure 80).[114] The ethylene undergoes trimerization to hexene, followed by disproportionation to hexane and 2,4-hexadiene, and a Diels−Alder reaction of 2,4-hexadiene with ethylene to give 3,6-dimethylcyclohexene. The latter is dehydrated to *p*-xylene. The disproportionation shows poor 2,4-hexadiene selectivity, but an iridium-based catalyst at 180 °C achieved a TON of 777 over 3.5 h (Table 18, entry 31).[788] A one-pot diene formation and Diels−Alder cyclization achieved 66% 3,6-dimethylcyclohexene selectivity, and dehydrogenation with $Pt/Al_2O_3$ yielded 93% *p*-xylene, giving an overall yield of 89%. While bio-ethylene is expected to become cheaper, significant research is required to increase the reaction efficiency and use heterogeneous catalysts.

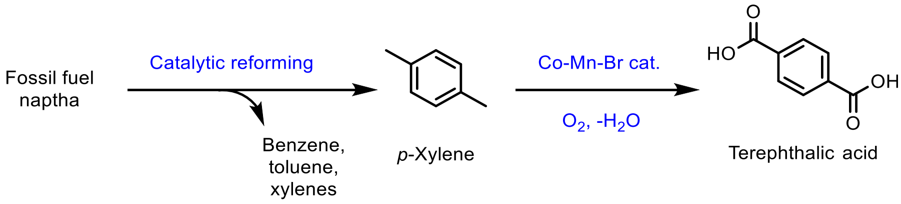


**Figure 79.** Conventional production of terephthalic acid from fossil fuel naphtha, *via p*-xylene.

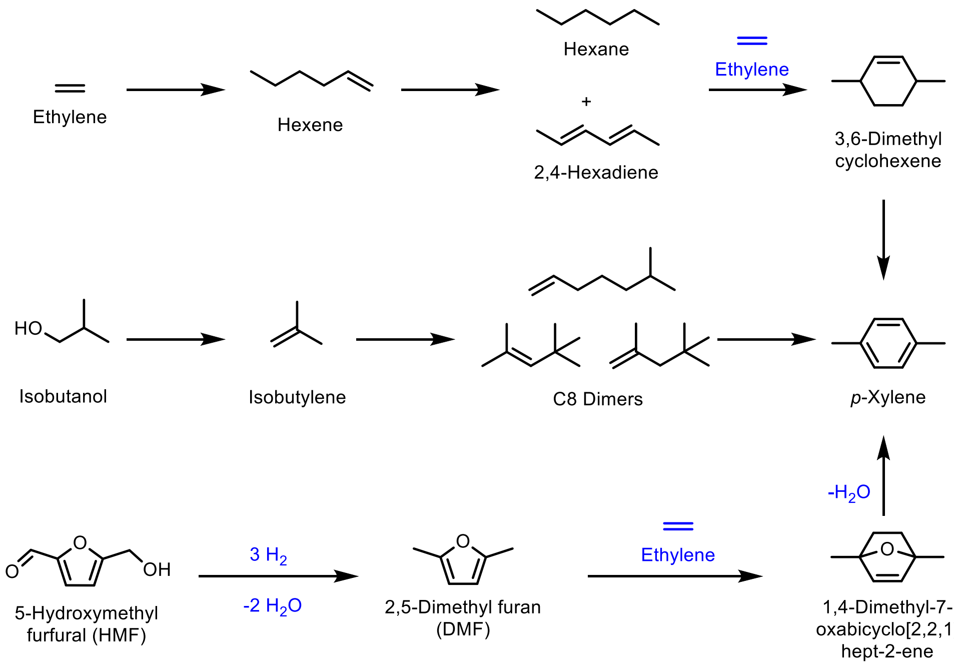


**Figure 80.** Established routes to bio-based *p*-xylene from ethylene, *iso*-butanol and 5-hydroxymethyl furfural (HMF).

Isobutanol, which can be produced *via* starch fermentation, has been studied as a feedstock for *p*-xylene production and commercialized by Gevo Inc.[789,974] Isobutanol is dehydrated to isobutylene with a BASF-AL3996 catalyst at 350 °C, oligomerized to di-isobutylene with a ZSM-5 catalyst, and converted to *p*-xylene with a $CrO_x$-doped-$Al_2O_3$ catalyst (Figure 80, Table 18, entry 32). The respective yields of the three steps are 95, 89 and 75%, giving an overall total yield of 63%. Starch is an expensive feedstock of isobutanol, constituting 46% of the operating cost, and the development of catalysts for the conversion of cheaper lignocellulosic biomass is required.[731,975]

2,5-Dimethylfuran (DMFu) can be produced from carbohydrates and can undergo Diels–Alder coupling with ethylene, followed by dehydration, to give *p*-xylene (Figure 80).[976] A dealuminated commercial H-Beta zeolite catalyst gave 99% conversion and a *p*-xylene yield of 97%, attributed to a balanced Brønsted/Lewis acid ratio of 2.3.[977−980] However, the microporous nature of the zeolite catalysts lead to pore blockage, coke formation and consequential catalyst deactivation.[981] Doping with $\gamma$-$Al_2O_3$ maintained a 97% *p*-xylene yield and decreased the coke deposit on the H-Beta catalyst from 12 to 7 wt %, but additional research into catalyst deactivation is important.[982] HMF can be converted into DMFu *via* hydrodeoxygenation and then converted to *p*-xylene *via* the aforementioned route.[983,984] A Pd-Au/$ZrO_2$ catalyst was reported to convert HMF to *p*-xylene *via* these steps, with a yield of 89% and significantly higher reusability than the aforementioned zeolite catalyst (Table 18, entry 33).[790] In 2013, Virent patented a heterogenous catalysis process for the derivation of ≥C8 hydrocarbons, including *p*-xylene, from biomass-derived sources.[985] Commercialized as BioFormPX, their bio-based *p*-xylene has been converted to PET *via* traditional methods and used in PET applications.[986,987]

Non-*p*-xylene routes to TPA are mostly from lignin or lignin-derived compounds. Lignin benefits from high aromatic content and extremely high renewable abundance, and many useful phenolics have been successfully obtained from lignin, including vanillin, vanillic acid, syringaldehyde and syringic acid.[988−990] While initial work focused on lignin oxidation treatment, recent advancements in catalytic transformation reveal that reductive lignin depolymerization gives aromatic monomers with much higher yields.[988,991−993] Corn-stover derived lignin oil was converted to phenolics *via* this route, and then transformed into TPA in 3 steps (Table 18, entry 34).[791] Demethoxylation with $MoO_x$/AC catalyst and subsequent carbonylation with a homogeneous Pd-based catalyst converted the phenolics into 4-alkylbenzoic acids, which were then oxidized to TPA with a $[Co(OAc)_2 + Mn(OAc)_2 + KBr]$ catalyst. While the TPA yield from was only 15.5 wt %, this is promising work for the valorization of cheap lignin. Glucose and glycerol were converted to isoprene and acrylic acid, respectively, and underwent cycloaddition catalyzed by $TiCl_4$ to give 4-methlycyclohex-3-enecarboxylic acid with a 90% yield (Table 18, entry 35).[792] This was then converted to TPA *via* vapor-phase aromatization and oxidation. Treatment of

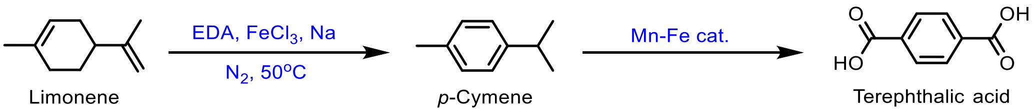


**Figure 81.** Conversion of bio-based limonene to terephthalic acid (TPA) *via* *p*-cymene.

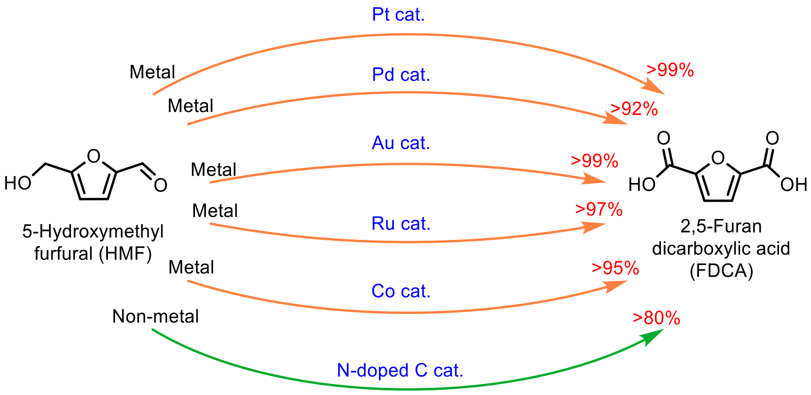


**Figure 82.** Most effective metal and non-metal catalyst types for the conversion of HMF to FDCA.

limonene, readily derived from citrus peel, with $FeCl_3$, ethylenediamine and sodium at 50 °C gave a 99% yield of *p*-cymene, which was then oxidized with a $MnO_x$-$FeO_x$ catalyst to give TPA with a yield of 51% (Figure 81, Table 18, entry 36).[793]

Current bio-based routes to TPA lack economic viability due to low yields, complicated procedures, feedstocks with limited supply and harsh reactions conditions.[731] Significant research into additional feedstocks and process integration to reduce purification steps are required before significant amounts of TPA from bio-sources will be produced.

2,5-Furandicarboxylic acid (FDCA), one of the top value-added chemicals derived from biomass, is produced on a 25 MT annum$^{-1}$ scale.[731,994] FDCA is anticipated to find applications in polyesters such as polyethylene 2,5-furanoate (PEF) as a substitute for the petrochemically derived TPA in polyethylene terephthalate (PET).[995] Consequently, FDCA synthesis from a range of feedstocks has been widely studied, with HMF emerging as currently the most suitable. Although reviewed in detail elsewhere,[731] a consolidated summary of the optimal results within each catalyst class from each feedstock is provided herein. Commercially, FDCA and subsequent polyesters of FDCA are produced by Avantium with their YXY catalytic Technology, predominantly from fructose.[996]

The majority of work in this area concerns the conversion of HMF to FDCA or its methyl diester, i.e., 2,5-furandimethyl carboxylate (FDMC), and several other feedstocks are converted *via* HMF.[809,997,998] A range of noble-metal based Pt, Pd, Au and Ru catalytic systems have been investigated, alongside several non-noble-metal based catalytic systems, with the catalytic performance significantly affected by the nature of their supports (Figure 82, Table 18, entries 37−51).[731] A Pt/N-doped-C catalyst without additive and a $Pt_5Bi_1/C$ catalyst with $Na_2CO_3$ additive produced FDCA from HMF with yields of 99+%.[795,999] Pd systems suffer lower selectivity than Pt, with FDCA yields of 92% using Pd/HT without additive and 93% using $Fe_2O_3$@HAP-Pd(0) with $K_2CO_3$.[731,796,797] Au catalytic systems are highly active for HMF oxidation in basic medium with high, with yields of >99% obtained using both Au/HY zeolite and $Au/Ce_{0.9}Bi_{0.1}O_2$ catalysts with NaOH as additive.[798,799] A Pd-Au catalyst had a synergistic effect on the conversion, with 100 FDCA% selectivity and yield of FDCA.[800] A $Au/CeO_2$ catalyst achieved a 99% yield of FDMC, the methyl diester of FDCA, due to the enhanced solubility of the methyl ester.[801] Ru offers an economical advantage over the other noble-metal systems, and affords moderate FDCA production both with and without base.[802,998,1000] A simple Ru/C catalyst with a $Mg(OH)_2$ additive and a $Ru/MnCo_2O_4$ catalyst without additives gave FDCA yields of 97 and 99%, respectively.[802,803] With Ru-based systems, an increase in productivity is observed with microwave heating.[1001] Several mixed metal oxides of non-noble metals including Cu, Ce, Mn and Co have also been proven effective at FDCA conversion from HMF, achieving yields 99+%.[804−806] A carbon nanotube-supported Co catalyst (Co-CN) used for FDMC production from a concentrated HMF solution (24%) gave a 95% yield (only 89% was isolated) and avoided the polymerization of HMF. Interestingly, a non-metal N-doped nanoporous-C catalyst with $K_2CO_3$ as an additive has also been used for HMF oxidation, with FDCA yields of 80%, albeit it with a low productivity.[808] Low productivity may be less of an issue for non-metal catalysts as lower prices enable higher catalytic amounts to remain cost-effective, especially if the non-metal catalysts can be produced sustainably.

Glucose and fructose have also been investigated as feedstocks for FDCA production (Table 19, entries 52−56).[809−812,997,998,1002,1003] Some studies simply convert the sugars to HMF, separate the HMF, and then convert it to FDCA, one-pot routes without the need to separate intermediates are advantageous with a view to industrial upscaling. A Pd/CC catalyst with acidic-$SO_3H$ sites was used to first dehydrate fructose to HMF under $N_2$, and then to convert HMF to FDCA with $K_2CO_3$ under oxygen, giving an overall yield of 64%.[809] Similar yields of 65% were reported both using Amberlyst-15 and Ru/C catalysts for the first and second steps, respectively, and using FDCA and Pt/C for the first and second steps, respectively.[810,811] Notably, the latter study utilizes the FDCA product as the acid catalyst. The highest reported yield of FDCA from fructose was performed using Amberlyst-15 and AuPd/HT in the first and third phase of a triphasic system for the dehydration and oxidation steps, respectively, yielding 78% FDCA (Figure 83).[812] Additionally,

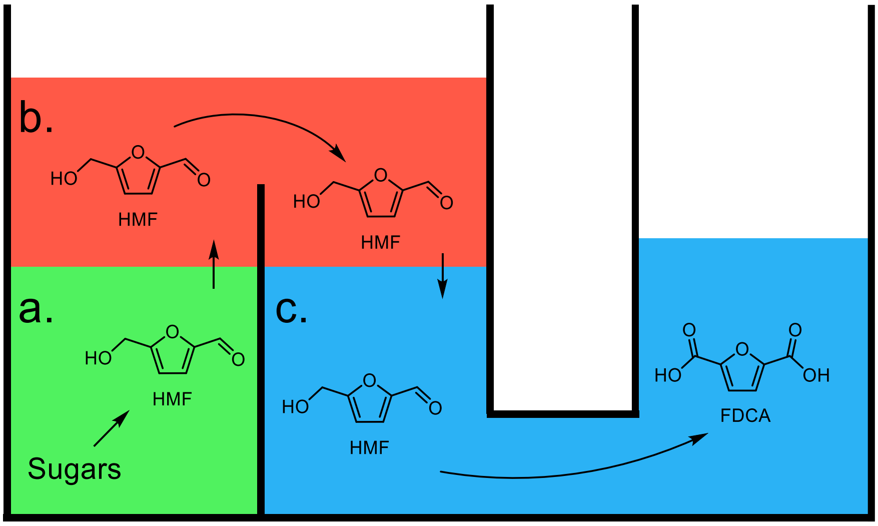


**Figure 83.** Conversion of glucose and fructose to FDCA *via* HMF in a triphasic system. (a) Phase 1: Tetraethylammonium bromide (TEAB), Amberlyst-15/$CrCl_3$, $H_2O$. (b) Phase 2: Methyl isobutyl ketone (MIBK). (c) Phase 3: $Au_8Pd_2$/HT, $Na_2CO_3$, $H_2O$.

the inclusion of $CrCl_3$ in the first phase enabled glucose to be used directly by first undergoing isomerization to fructose, achieving a 50% yield from glucose.

**5.1.2. Diols.** Diols are crucially important difunctional compounds for polymer synthesis due to their use in polyureas, polycarbonates and, in particular, polyesters. The wide availability, ease of synthesis and relative stability of hydroxy-functionalized chemicals have enabled the preparation of a plethora of diol compounds, although for the scope of this review only aliphatic diols are reviewed in detail (Figure 84). Beyond 4-carbon diols, only the production of $\alpha,\omega$-diol isomers are reviewed in the aliphatic part of the report, as the number of structural isomers grows exponentially with the number of carbons.

*5.1.2.1. C2 Diol.* Ethylene glycol (EG, 1,2-ethanediol), largely used for the production of anti-freeze liquids and polyethylene terephthalate (PET), is predominantly made from petrochemical ethylene.[1004,1005] Ethylene is oxidized to ethylene oxide with a Ag catalyst, and subsequently hydrated to EG in the presence of a catalyst, such as a solid acid.[1006,1007] In recent years, there has been significant progress on utilizing renewable feedstocks for ethylene glycol synthesis, both *via* chemical transformations and *via* biotechnological routes.

The dominant route to biomass-derived EG involves the drop-in of biomass-derived ethylene to the conventional route.[1008,1009] Biomass-derived ethylene is predominantly produced *via* the fermentation of sugar to ethanol and the subsequent dehydration to ethylene (see section 2.1). A direct route *via* the hydrogenolysis of sugars suffers from poor EG selectivity, coyielding propylene glycol (PG) and glycerol as other valuable side products (Figure 85).[1010,1011] The EG selectivity from sugar has been improved to 76% with a tungsten based catalyst.[1012,1013] Cellulose can also be converted to EG *via* hydrolysis to glucose, retro-aldol condensation to glycolaldehyde, and finally hydrogenation to EG (Figure 85).[1014−1017] An acidic aqueous solution at ~250 °C and under high pressure, is used for the hydrolysis, with the 2nd and 3rd step using a tungsten-based and Raney-Ni catalyst, respectively. EG yields above 75% are reported for the hydrogenolysis of pure cellulose (Table 20, entries 1−3), while yields from pre-treated lignocellulosic biomass under similar conditions have 64% (Table 20, entries 4 and 5).[1018,1019] Cellulose directly from pre-treated lignocellulosic biomass with 39% lignin content gave an EG yield of 35%, with the lignin found to not significantly retard the reaction, as was expected elsewhere (Table 20, entry 6).[1020−1022]

Direct cellulose conversion brings with it difficulties in handling solid cellulose and the need for catalysts capable of performing multiple reactions.[1011] As such, the direct conversion of sugars to EG has been investigated under similar conditions, benefiting from higher feasible feedstock concentrations (up to 35 wt %) and enhanced catalyst lifetime in the absence of typical lignocellulosic impurities (Table 20, entries 7−9).[1023−1026] However, EG yields from sugar hydrogenolysis exceeding 60% have yet to be reported, while reported yields from cellulose are higher.[1027] The counter-intuitive higher yield obtained from cellulose was attributed to the slow cellulose hydrolysis reaction preventing a build-up of sugars prior to the slow retro-aldol reaction, which otherwise would result in the production of sorbitol and other side-products. Ooms *et al.* achieved an EG productivity of 300g $L^{-1}$ $h^{-1}$ with a yield of only 36 wt %, suggesting that the ease of operation somehow compensate for the lower yields. While less studied, biomass hydrolysates are a more pragmatic feedstock than glucose, and corn stover hydrolysates were converted to EG with a cheap Raney-Ni/NaOH catalyst system with a mass yield of 0.19 g $g^{-1}$ (Table 20, entry 10). Compared to the best-reported glucose conversion to EG (mass yield of 0.62 g $g^{-1}$) using a Ni/W catalyst, this reasonably high 0.19 g $g^{-1}$ yield is promising.[1024,1025]

EG is also produced as a side product during glycerol hydrogenolysis toward 1,2-propanediol, with increased reaction temperatures to 300 °C enabling EG yields up to 37 mol %, albeit with increased side product formation (Table 20, entry 11).[1028,1029] However, the separation of EG is difficult and most studies optimize the process to reduce EG production, so glycerol hydrogenolysis is unlikely to develop as a route to sustainable EG.[1030,1031]

In 2019, Avantium completed the construction of a demonstration plant for the one-step conversion of glucose to EG using a Ru-$H_2WO_4$ catalyst system with a promotor metal.[1032,1033] Interestingly, 1,3-butanediol is also produced as

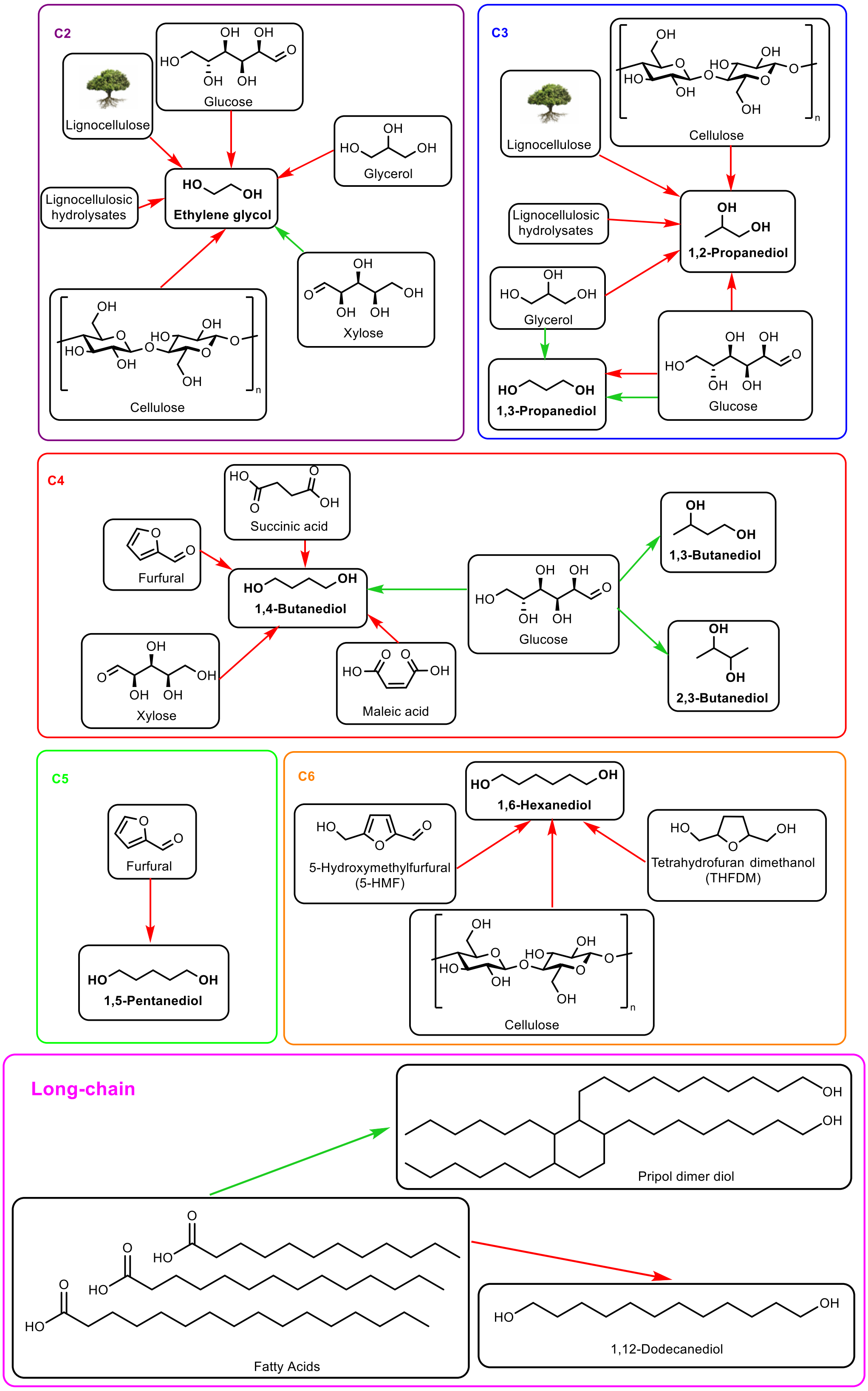


**Figure 84.** Summary of the chemical (red arrows) and biotechnological routes (green arrows) to short chain aliphatic organic diols from biomass sources.

a side-product, which could be separated *via* azeotropic distillation. In 2021, a collaboration between Braskem and Haldor Topsoe also resulted in the completion of a demonstration plant for EG production from glucose using patented MOSAIK technology (Table 20, entry 12).[1034−1036] The three-step process begins with the pyrolysis of a sugar solution to predominantly glycolaldehyde at >500 °C, and then hydrogenating those compounds with Cu/C at 230 °C

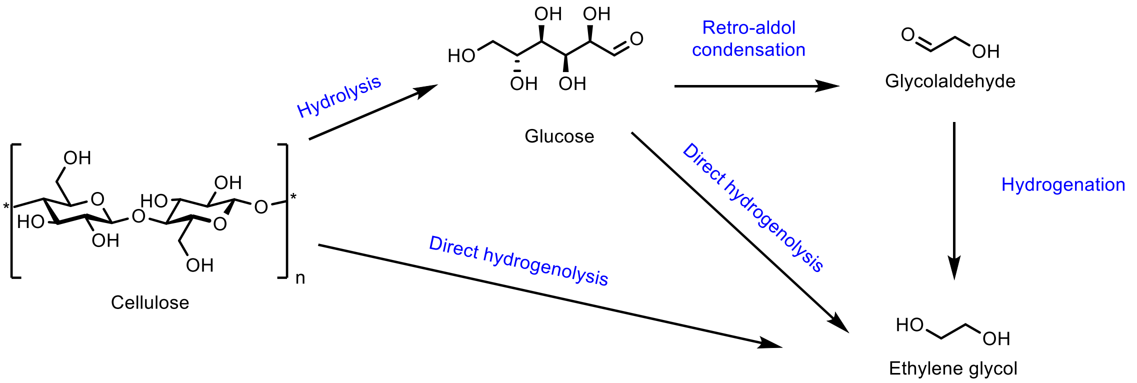


**Figure 85.** Conversion of cellulose and glucose to ethylene glycol (EG). Cellulose can be converted in a three-step procedure or *via* direct hydrogenolysis. Glucose is an intermediate of the direct hydrogenolysis pathway and can be used directly as a feedstock for direct hydrogenolysis to EG.

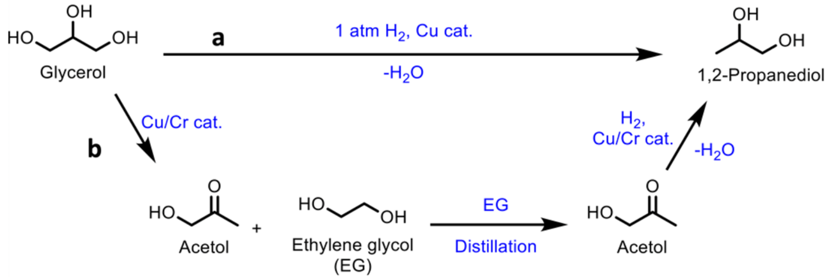


**Figure 86.** Hydrogenolysis of glycerol to 1,2-propanediol *via* (a) a single-step approach, or (b) a two-step approach utilizing the difference in boiling point to remove the EG by-product before conversion of acetol to 1,2-PDO.

followed by Ru/C at 80 °C, in the gas and liquid phase, respectively.[1035,1037] The inventors report a combined yield of the hydrogenation steps of >98%, and expect a commercial plant production by 2023.[1028,1036] The amount of current investments in producing EG from sugars suggests that this route has been deemed economically viable, but the field of EG production would benefit from continued research into improved catalysts, particularly for more realistic feedstocks such as lignocellulosic hydrolysates.

There are no natural biological pathways to synthesize EG directly from glucose, although engineering microbes enables some biotechnological routes to EG (bio-EG) from xylose.[1038] Metabolic simulations supported the engineering of an engineered *E. coli* strain that achieved a titer of 108.2 g $L^{-1}$ EG at a yield of 0.36 g $g^{-1}$ xylose, the highest titer thus far reported from xylose (Table 19, entry 6).[852] Two additional pathways have been proposed, both of which pass through glycolaldehyde and dihydroxyacetone phosphate, with the second pathway also including an initial epimerization of D-xylulose to D-ribulose.[853,1039] Optimization of the two routes yielded titers of 20 and 40 g $L^{-1}$ of EG, respectively, with yields of 0.38 and 0.35 g $g^{-1}$ xylose, respectively (Table 19, entry 7). The carbon utilization of these pathways is limited to 40% as the 5-carbon pentose is converted into a 2-carbon glycolaldehyde and a 3-carbon intermediate, with only the former converted into EG.[1038] The combination of these pathways with a serine synthesis pathway allows utilization of the 3-carbon intermediates to produce additional glycolaldehyde, doubling the maximum total conversion of pentose carbon to 80%, but this requires significant further work.[1040−1042] A recent study produced bio-EG from glycerol *via* an enzymatic cascade through glycolaldehyde, and yielded 0.52 g EG/g glycerol, the highest reported yield from any route to date.[1043] The current price of EG is low due to established large scale industrial production, and titers and yields of EG should exceed 100 g $L^{-1}$ and 0.5 g $g^{-1}$ feedstock before presenting bio-EG as a competitive alternative.

*5.1.2.2. C3 Diols.* The two propanediol isomers, 1,2-propanediol (1,2-PDO; propylene glycol) and 1,3-propanediol (1,3-PDO; trimethylene glycol) are industrially important chemicals commonly used in polymer synthesis to make unsaturated polyester resins and polytrimethylene terephthalate, respectively. Many studies have investigated to both 1,2-PDO and 1,3-PDO from biomass feedstocks such as glycerol, glucose and cellulose, both *via* chemical and biotechnological routes.

1,2-PDO is readily produced via the selective catalytic hydrogenolysis of glycerol, a route that is well established as it can be integrated with waste glycerol produced during the transesterification of fatty acids for biodiesel production (Figure 86).[1058] Glycerol hydrogenolysis produces a range of C2 and C3 alcohols and diols, including EG, and 1,3-PDO, but has the highest selectivity for 1,2-PDO. Hence, glycerol hydrogenolysis is typically studied to maximize 1,2-PDO selectivity and yield. A 1,2-PDO yield of 85% was obtained from glycerol *via* hydrogenolysis at 230 °C with a Ru/Cu-modified bentonite catalyst (Table 20, entry 13).[1029] The Archer Daniels Midland Company (ADM) and Oleon/BASF have both commercialized 1,2-PDO production from biodiesel-derived glycerol, with annual production capacities of 100 and 20 kt 1,2-PDO, respectively.[1059,1060] ADM reported a 61% reduction in greenhouse gas emissions, compared to the petrochemical route.[1059] Glycerol hydrogenolysis typically occurs either in a single, high temperature step that encourages glycerol conversion at the cost of reduced 1,2-PDO selectivity, or *via* a patented two-step approach (Figure 86a,b, respectively).[1061,1062] In the latter route, glycerol is converted to acetol at high temperature and reduced pressure and then hydrogenated at a lower temperature and higher hydrogen pressure.[1062] The EG side product is removed before the hydrogenation step due to the separation of EG from acetol being significantly easier than from 1,2-PDO, and the hydrogenation step requires $H_2$/glycerol ratios lower than 15, hence reducing production costs.[1062] A fixed-bed reactor with a 130−200 °C temperature gradient and Cu catalysts achieved a similar effect, albeit without the intermediate removal of EG, and obtained a 1,2-PDO yield of 0.79 g $g^{-1}$.[1061] However, the scalability of this system is questionable due to both the high $H_2$/glycerol ratio used (i.e., 140:1) and the exothermicity of the overall reaction, so the two-step process currently appears to be the most pragmatic route.

Since $H_2$ production often relies on either petrochemical sources or energy-intensive processes, some studies have investigated glycerol hydrogenolysis without external $H_2$, but estimated 1,2-PDO costs were 2-3 times higher and the estimated environmental impact was even greater than the petrochemical route.[1011,1058,1063] This area has benefitted from significant research in recent years, but further study to achieve lower $H_2$ requirements, catalysts for utilizing raw glycerol and improved separation procedures are all required for increased commercialiity.

1,2-PDO can also be produced from cellulose and glucose feedstocks, as long as an isomerization of glucose to fructose takes place prior to hydrogenolysis, typically with a basic catalyst.[1011] Similar yields and productivities are reported using various different catalytic systems, including Cu-$WO_x/Al_2O_3$, Pd-$WO_x/Al_2O_3$ and CuCr in the presence of $Ca(OH)_2$.[1047,1064,1065] Xiao *et al.* reported the highest 1,2-PDO yield from both glucose and cellulose by hydrogenolysis (53 and 42%, respectively) *via* first converting the feedstock to sorbitol or mannitol at 140 °C and then converting to glycols under pressurized $H_2$ and in the presence of $Ca(OH)_2$ and CuCr (Table 20, entries 14 and 15).[1047,1048] Directly using lignocellulosic sources presents a more realistic use-case, with a 1,2-PDO yield of 39% achieved with a Ni-$W_2C$/AC catalyst from a Jerusalem artichoke feedstock, comparable to the results with purified cellulose (Table 20, entry 16).[1049] Similarly, hydrogenolysis of lignocellulosic hydrolysates with Raney-Ni and NaOH produces 1,2-PDO as the major product with a yield of 41% (Table 20, entry 17).[1025]

Besides catalytic chemical routes, several microbes naturally produce 1,2-PDO (bio-1,2-PDO) from L-rhamnose or L-fucose, although these carbon sources are considered too expensive for commercial viability.[1066] Alternatively, dihydroxyacetone phosphate can be converted to bio-1,2-PDO *via* methylglyoxal, and can be produced from a range of sustainable feedstocks including sugars, glycerol or $CO_2$.[1067−1069] The reductant coenzyme-1 (NADH) is consumed to produce 1,2-PDO from glucose or glycerol, so co-production of 1,2-PDO with NADH-generating acetate production was engineered and optimized to give a titer of 0.59 g $L^{-1}$ and a 1,2-PDO yield of 0.48 g per gram glucose.[1067,1070,1071] To reduce the effect of toxic intermediates, zinc finger enzyme scaffolds and microcompartments have been investigated, which increased 1,2-PDO yields by 350% and 250%, respectively, relative to the free-enzyme strain.[1072,1073] $CO_2$ has been also been converted into 1,2-PDO in *S. elongatus*, although titers are very low (i.e., <0.2 g $L^{-1}$). Interestingly, engineered *E. coli* can produce enantiomerically pure (>98% ee) *R*- and *S*-1,2-PDO from D- and L-lactate, respectively, *via* a non-methylglyoxal-dependent pathway, with titers of 1.5−1.7 g $L^{-1}$.[1074] The titers and yields of bio-1,2-PDO are much lower than those of biotechnologically produced 1,3-PDO, while commercial 1,2-PDO is cheaper than 1,3-PDO. Significant further research is required for feasible commercialization of bio-1,2-PDO, but enantiomerically pure 1,2-PDO could provide interesting polymer possibilities, as tacticity influences physical polymer properties.

Research into bio-based 1,3-PDO production focuses on the conversion of glycerol (Figure 87). While catalytic studies focus on utilizing more concentrated, purer glycerol feedstocks to prevent catalyst deactivation, fermentative conversion has been more successful with raw glycerol streams due to high enzyme selectivity.[1075,1076] The hydrogenolysis of glycerol to produce 1,3-PDO usually proceeds at 140−200 °C, with 40−80 bar $H_2$, over a Pt catalyst, with 1,3-PDO yields in the range of 0.2−0.4 g $g^{-1}$ and selectivity of 30−71%.[1011] Most catalysts for glycerol hydrogenolysis produce 1,2-PDO with much higher selectivity than 1,3-PDO, unless the temperature, glycerol concentration, or $H_2$ pressure are increased.[1011,1051,1077,1078] The highest yield obtained in batch operation, 66% and 0.55 g $g^{-1}$, utilized a dilute glycerol solution and a Pt/$WO_x$/AlOOH catalyst, but required 50 bar $H_2$ and energy intensive separation and/or purification steps (Table 20, entry 18).[1050] Contrastingly, continuous operation at atmospheric pressure over a zeolite Pt-Cu catalyst has achieved yields of 53% and 0.45 g $g^{-1}$ (Table 20, entry 19).[1051] Despite the slightly lower yields, the milder conditions, more concentrated feed and continuous nature of the process presents the best current option for commercial 1,3-PDO production *via* catalytic glycerol hydrogenation. Although yields remain lower than for 1,2-PDO, the higher selling price of 1,3-PDO could result in commercial viability.[1011,1079]

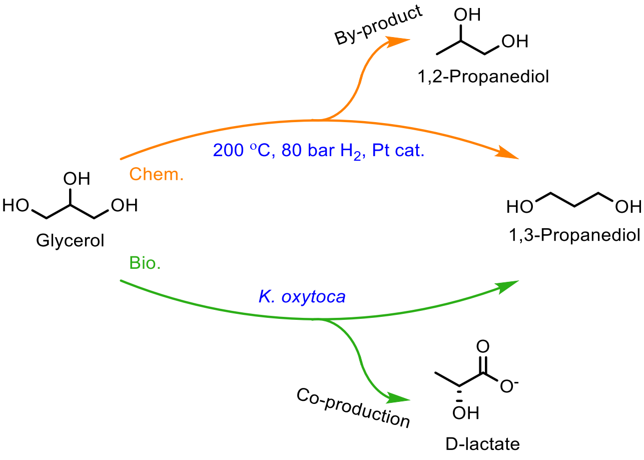


**Figure 87.** Chemical and biotechnological routes to 1,3-propanediol from glycerol. The chemical hydrogenolysis requires elevated temperatures and pressures to reduce the amount of the 1,2-Propanediol by-product product. The biotechnological route performs best with the coproduction of D-lactate, due to the balancing of oxidative and reductive pathways.

Bio-1,3-PDO is naturally produced from glycerol by several microbes, *via* dehydration to 3-hydroxypropionaldehyde (3-HPA) and then reduction to 1,3-PDO.[1080−1083] The reductant,

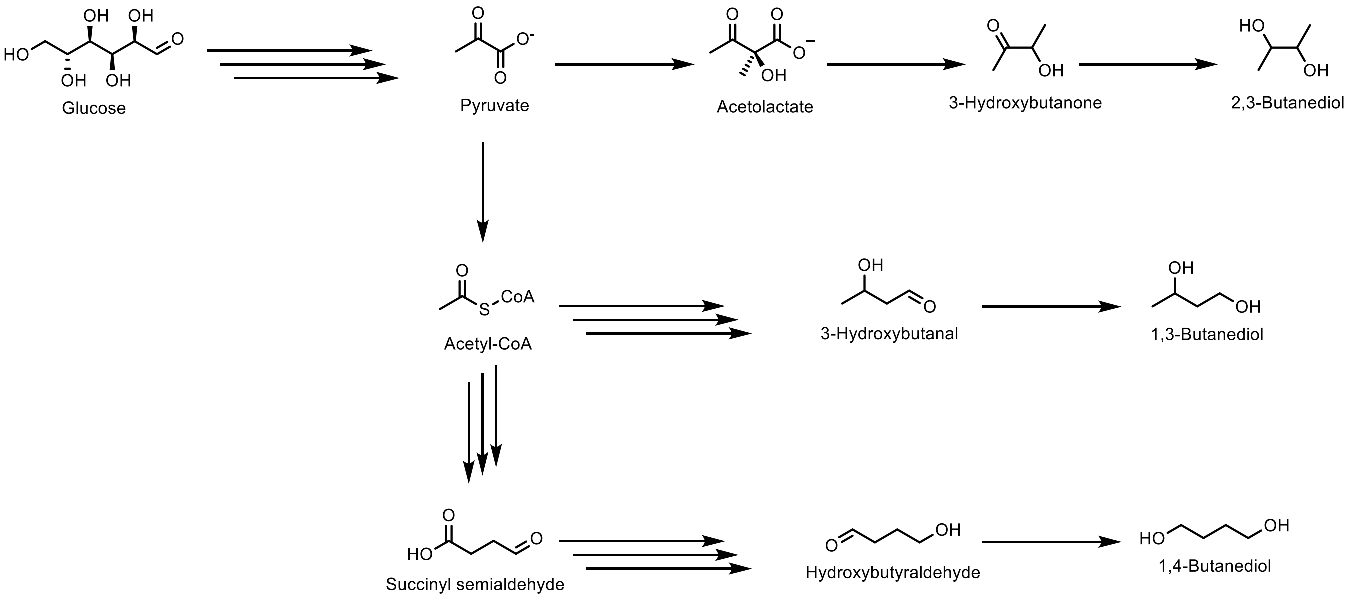


**Figure 88.** Synthesis pathways of butanediols starting from glucose.

NADH, is typically regenerated *via* the glycerol oxidation pathway, producing several natural by-products.[1084] Most previous strategies sought to optimize 1,3-PDO synthesis from glycerol by blocking one or some of the by-product synthesis pathways, but this proved ineffective at increasing yields as one oxidative pathway is required to enable NADH regeneration.[853,1085−1089] Instead, the coproduction of 1,3-PDO and another valuable NADH-regenerating chemical has been conducted and an engineered *Klebsiella oxytoca* has produced 76 g $L^{-1}$ 1,3-PDO and 112 g $L^{-1}$ D-lactate at a 95% conversion yield from glycerol (Table 19, entry 8).[854,1090,1091] From glycerol and glucose as cosubstrates, parallel pathways in an engineered *C. glutamicum* generated 1,3-PDO and glutamate, respectively, with NADH consumed in the former pathway and regenerated in the latter.[1091] The 1,3-PDO yield was extremely high (~1.0 mol/mol glycerol) and the glutamate yield was higher than in the industrial glutamate-producing strain. D-Lactate and glutamate can be easily separated from 1,3-PDO, evidence that coproduction processes are promising for the future of efficient, cost-effective biorefineries.[1038] Further, an engineered *K. pneumoniae* produced 1,3-PDO and 3-HP at a yield of 82%, with an additional supply of $B_{12}$.[1090]

While there are no natural pathways directly to 1,3-PDO from sugars, engineered microbes can combine the glucose-to-glycerol and glycerol-to-1,3-PDO pathways to produce 1,3-PDO from glucose.[1038] Using engineered *E. coli.*, DuPont have achieved a titer of 135 g $L^{-1}$ of 1,3-PDO from glucose, although the pathway requires additional $B_{12}$ (Table 19, entry 9).[855,1092] A proposed non-natural route to circumvent the $B_{12}$ requirement utilizes homoserine as a precursor and can use simple media.[1093] Since serine synthesis pathways are established, the two routes could be effectively integrated to give up to 1.5 mol 1,3-PDO per mole glucose without the need for $B_{12}$ supplementation.[1094−1096] While Bio-1,3-PDO has been commercialized, wide adoption is limited by the relatively high price, partly due to the low price of crude glycerol.[1038] Additionally, implementation of $B_{12}$-avoiding pathways can significantly reduce the production cost of Bio-1,3-PDO.

*5.1.2.3. C4 Diols.* There are four butanediol isomers, 1,2-BDO, 1,3-BDO, 2,3-BDO and 1,4-BDO, which all show industrial applications. 1,4-BDO is most important as a monomer and solvent, and an annual production of 2 million ton.[1097] 2,3-BDO is considered as a potential platform chemical, 1,3-BDO is a widely used solvent and 1,2-BDO finds use in polyester resins.[1098−1101] The majority of work on the production of butanediols study biotechnological routes. Bio-1,4-BDO production has been reviewed in depth elsewhere.[597,1038] 1,4-BDO is predominantly produced *via* hydrogenation of butynediol, acetoxylation of butadiene and hydrogenation of maleic anhydride, with the last route attracting interest due to its operational safety advantages and possible integration with sustainable maleic anhydride production (Figure 88).[1102] The hydrogenation of maleic anhydride or maleic anhydride-derived dialkyl esters *via* a $\gamma$-butyrolactone (GBL) intermediate has been conducted with noble-metal and Cu-based catalysts, with 1,4-BDO selectivity above 66% (Table 20, entry 20).[614,1052,1103] 1,4-BDO has also been obtained from several renewable platform molecules, including succinic acid (SA) and furfural, although the 2 Mt $annum^{-1}$ scale of 1,4-BDO production far exceeds that of both SA and furfural, at 60 and 604 kt $annum^{-1}$, respectively (Table 20, entries 21 and 22).[580,583,1054,1104−1109] If produced sustainably on a larger scale, these feedstocks could provide pragmatic routes to 1,4-PDO. A range of noble metal catalysts for the direct hydrogenation of SA have been investigated, with a Re/Pd catalyst giving the highest 1,4-BDO yield of 66%.[580,583,1053,1106,1108,1109] The oxidation of furfural yields SA, maleic anhydride, and 2(5*H*)-furanone, which can all be converted to 1,4-BDO *via* GBL and a two-step oxidation of furfural over a $Pt/TiO_2$-$ZrO_2$ catalyst with 85% 1,4-BDO yield.[818,1054,1107,1110,1111]

A highly engineered *E. coli* strain produces a 1,4-BDO titer and yield of over 120 g $L^{-1}$ and 80% from glucose (Table 19, entry 10).[597] An alternative pathway from xylose yielded 12 g $L^{-1}$ with glucose as a cosubstrate (Table 19, entry 11).[856] While the yields from xylose are much lower than from glucose, using non-food sugars can help to avoid food supply conflicts, and similar pathways can be engineered from other

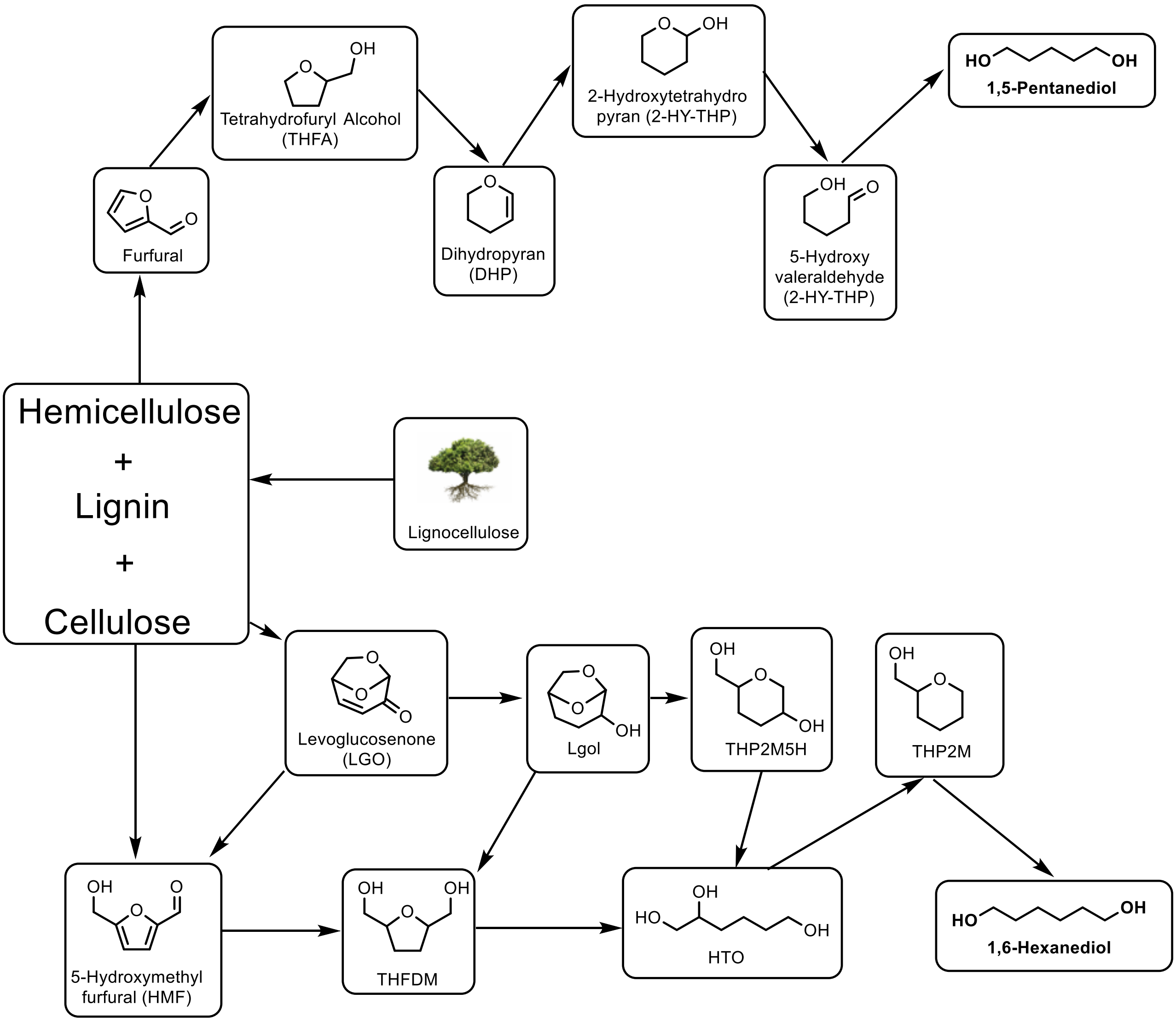


**Figure 89.** Simplified reaction scheme for the combined production of 1,5-pentanediol (1,5-PeDO) and 1,6-hexanediol (1,6-HDO) from lignocellulose, as present by He *et al.*

non-food sugars.[856] In 2020, a biorefinery modelled by De Bari *et al.* estimated the conversion of 60 kt annum$^{-1}$ residual lignocellulosic biomass to 8 kt annum$^{-1}$ of 1,4-BDO, with the energy generated from secondary streams capable of sustaining 78% of the total electricity demand.[1112] 2,3-BDO is produced naturally by various microorganisms and exists as a mixture of three stereoisomers.[1113−1117] No non-natural pathways have been proposed, but wild-type microorganisms such as *K. pneumoniae* can produce titers of 150 g L$^{-1}$ 2,3-BDO from glucose, and strain engineering has increased the molar yield to 96% (Table 19, entry 12).[857,1038,1070,1118] Enantiopure stereoisomers of 2,3-BDO have also been investigated, with *S. cerevisiae* yielding titers of over 100 g L$^{-1}$ (2*R*,3*R*)-BDO from a mixture of glucose and galactose, two major components of red algae.[1119] Pilot scale production of 2,3-BDO and coproduction of 2,3-BDO with 1,3-PDO have been demonstrated.[1120] The remaining BDOs are not produced naturally, but pathways to 1,4-BDO and 1,3-BDO have been proposed in recent years and the biotechnological production of 1,4-BDO has been commercialized by Genomatica.[916,1097,1101,1121] A 4-step pathway from glucose to 1,3-BDO in engineered *E. coli* and gave a titer and yield of 15.7 g L$^{-1}$ *R*-1,3-BDO (98% ee) and 37%.[1101,1122] Optimizations including the conversion of a byproduct into desired 1,3-BDO, increased the molar yield to 57% (Table 19, entry 13).[858] To date, no metabolic pathways to synthesize 1,2-butanediol have been reported.

*5.1.2.4. C5 Diol.* 1,5-Pentanediol (1,5-PeDO) is produced on a 3 kt annum$^{-1}$ scale, with a consequentially high \$6000 ton$^{-1}$ market price, three times higher than that of the shorter alkyl spaced 1,4-BDO, due to limited accessibility of C5 petrochemical feedstocks.[1123] 1,5-PeDO is currently produced through the hydrogenation of glutaric acid, which is produced from acetylene and formaldehyde *via* the 1,4-butynediol intermediate.[1124,1125] 1,4-butynediol undergoes hydrogenation to 1,4-butanediol, dehydration to GBL, ring opening with potassium cyanide, and finally hydrolysis to glutaric acid. This route suffers from multiple steps, toxic chemicals such as potassium cyanide, and relies on petrochemical feedstocks. Research into 1,5-PeDO production from biomass sources has focused on the selective hydrogenolysis of tetrahydrofurfuryl alcohol, which is produced *via* Ni- or Cu-catalyzed hydrogenation of the platform chemical furfural.[1126−1128] The

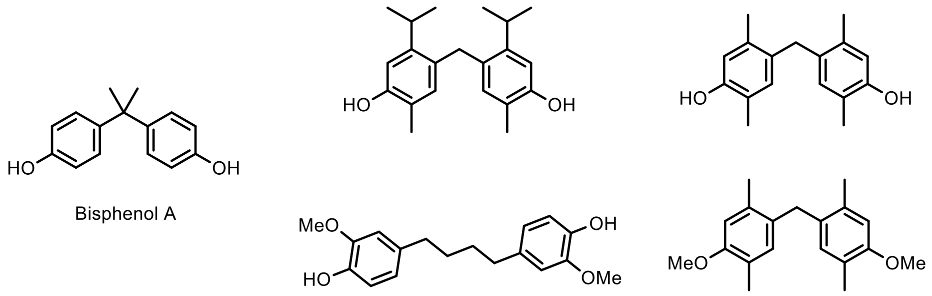


**Figure 90.** Bisphenol A (BPA) and a series of bio-based bisphenol alternatives with lower toxicity.

hydrogenolysis is conducted over bimetallic noble metal catalysts, but the catalysts are expensive and have low activities.[1055] He *et al.* demonstrated a multi-step process to produce PeDO from furfural with a sequential dehydration-hydration-hydrogenation route *via* tetrahydrofurfuryl alcohol, dihydropyran (DHP), and 2-hydroxytetrahydropan (2-HY-THP) (Figure 89, Table 20, entry 23).[1055] The overall process has a 1,5-PeDO yield of 80% from furfural, and a modelled pathway from white-birch lignocellulose estimated a 1,5-PeDO selling price of ~\$4000 ton$^{-1}$, a reduction of ~33% from current 1,5-PeDO prices.[1055]

*5.1.2.5. C6 Diol.* 1,6-Hexanediol (1,6-HDO) is currently produced on a scale of 130 kt annum$^{-1}$, with a market value of ~\$4400 t$^{-1}$, *via* the catalytic reduction of adipic acid (AA) or its esters over Cu-, Co- or Mn-based catalysts, at ~200 °C and 150−300 bar $H_2$.[1055,1123] While AA is currently produced from petrochemical (section 5.1.1.4), the scale of AA production (3 Mt annum$^{-1}$) dwarfs that of 1,6-HDO, and any transition to sustainable AA production would enable direct substitution into 1,6-HDO production. Furthermore, many of the mentioned routes to bio-based AA had impurities rendering them unsuitable for nylon production, but not necessarily unsuitable for use in applications such as 1,6-HDO production.

A three-step process for 1,6-HDO production from biomass *via* hydrolysis/dehydration to HMF with dilute acid, hydrogenation to tetrahydrofuran dimethanol (THFDM) over Raney-Ni, and hydrogenation to 1,6-HDO with $Cu_2Cr_2O_5$ was patented in 1983.[1129] In the years since, several studies have reported conversions from HMF or one of the other intermediates.[1056,1130,1131] A 1,6-HDO yield of 58% directly from HMF was achieved with expensive Pd/$SiO_2$ and Ir-Re$O_x$/$SiO_2$ catalysts (Table 20, entry 24).[1056] A high yield of 83% 1,6-HDO from levoglucosenone (LGO)-derived THFDM was reported in a DuPont patent using Pt$WO_x$/$TiO_2$ at 160 °C and 5.5 MPa $H_2$ (Table 20, entry 25).[1057] He *et al.* reported a multi-step catalytic process for the production of 1,6-HDO from cellulose (Figure 70, Table 20, entry 26).[1055] In the process, LGO and HMF were obtained from cellulose, converted to THFDM *via* hydrogenation and hydrogenolysis with Ni- and Pd-based catalysts, and converted to 1,6-HDO by hydrogenolysis of THFDM with a Pt-based catalyst.[1132,1133] A combined LGO and HMF yield of 48% was achieved from cellulose with dilute sulfuric acid in a 99:1 THF/$H_2O$ mixture. LGO and HMF were converted to LGOL and THFDM, respectively, at 100 °C using Ni/$SiO_2$ with near-quantitative yields, and then further converted at 150 °C with Pd/Si-Al, where LGOL underwent hydrogenolysis to THFDM with a selectivity of 63%. Overall, the selectivity of the LGO+HMF conversion to THFDM was 83%, but the total selectivity toward 1,6-HDO was estimated to be 94%, due to the conversion of an additional intermediate, THP2M5H, to 1,6-HDO *via* ring opening followed by the same steps as with THFDM. The THFDM, and THP2M5H, then underwent hydrogenolysis to HTO and conversion to 1,6-HDO in a batch reactor at 160 °C and 5.5 MPa $H_2$, with a Pt-based catalyst and an overall 1,6-HDO yield of >70% from HMF. A modelled pathway from white-birch lignocellulose estimated a 1,6-HDO selling price of ~\$4000 ton$^{-1}$, a similar price to 1,6-HDO derived from petrochemical sources.[1055] Recently, Kim *et al.* presented the modelling of a similar multi-step process, with the final 1,6-HDO selling price estimated at \$4700 ton$^{-1}$ if the overall product yield can be increased from 23% to 40%, which is an estimate in quite good agreement with the work of He and co-workers.[1055,1134]

*5.1.2.6. Long-Chain Diols.* The biotechnological production of C8−C16 $\alpha,\omega$-diols ($\alpha,\omega$-DOs) from renewable fatty acids has been conducted with modified *E. coli*, *via* $\omega$-oxidation of fatty acids to $\omega$-hydroxy fatty acids and their subsequent reduction.[1135] The obtained $\alpha,\omega$-DOs yield peaked at 5 g L$^{-1}$ at 96% conversion for the production of 1,12-dodecanediol, a 66-fold increase since biotechnological 1,12-dodecane was first reported in 2006.[1135,1136] Croda produce a diacid from dimerizing unsaturated fatty acids (cf. section 5.1.1.5), which has been converted to diol and commercialized under the brand name Pripol (Figure 78b).[967] As well as simple aliphatic diols, low-molecular weight hydroxyl-terminated polymers are often used as diols in step-growth polymerizations, including for polyurethane and polyurea formation but can also be employed for the synthesis of other polymer classes, e.g., polyethers, polyesters and polycarbonates. Although conventionally petrochemically sourced, oligomeric/polymeric diols have been produced from biomass sources including lignin, terpenoids, corn and soybean oil, as has been recently reviewed in detail by Gupta *et al.* and Sardon *et al.*[1137,1138]

*5.1.2.7. Aromatic Diols.* Aromatic diols, typically referred to as bisphenols, are aromatic structures with 2 hydroxy groups attached to aromatic structures. Bisphenol A (BPA) is a diphenylmethane derivative with two *para* hydroxy groups, and has been widely used in polymer synthesis, particularly in polycarbonates. BPA is produced *via* the solid-acid catalyzed hydroxyalkylation of acetone with excess phenol.[1139] As it is possible to produce both phenol and acetone from biomass, bio-based BPA can be produced from biomass *via* the current hydroxyalkylation route.[253,1140] However, BPA and residual phenol are very toxic and several substitutes to BPA have been proposed and studies. Some alternative petrochemical bisphenols such as bisphenol F (BPF) and bisphenol S (BPS) have been produced to avoid the growing body of legislation limiting BPA use, but these exhibit similar toxicity issues and

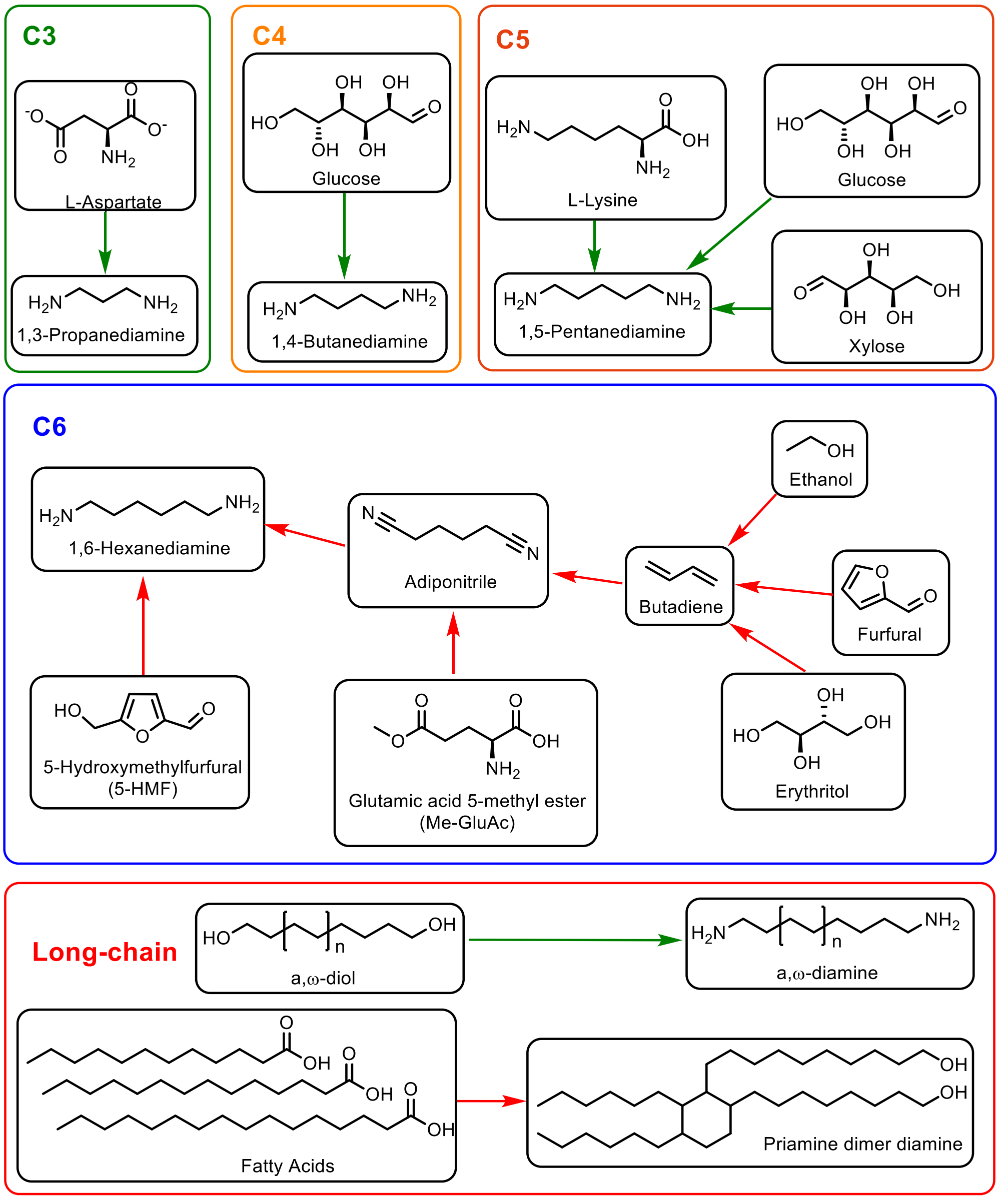


**Figure 91.** Summary of the routes to short chain aliphatic organic diamines from biomass sources, where chemical catalytic conversions are shown with red arrows and biotechnological conversion are shown with green lines.

may face similar legislative constraints in the near future.[1141−1144]

A lot of work has been completed to replace BPA with less-toxic bio-based monomers, as recently reviewed by Liguori *et al.*[1145] A wide range of aromatic or rigid cyclic diols have been produced from sustainable feedstocks including cellulose-derived glucose and HMF, lignin-derived phenolics, terpenes and citric acid.[1145] However, the lack of relevant safety data is not evidence of reduced toxicity, and these bisphenols are simply potential BPA substitutes until their toxicity can be studied. Garrison *et al.* produced a series of nine bis- and tris-phenols from a range of abundant aromatic biomass sources such as eugenol and creosol and found them to have lower toxicities than BPA (Figure 90).[1146] This area of research would benefit from similar work across the whole range of sustainably produced aromatic and rigid cyclic diols, proving their reduced toxicity, as well as work investigating the implementation of these monomers in polymers to determine if they are functional BPA replacements.

#### 5.1.3. Diamines.

Diamines are widely used in polymers classes such as polyamides and polyurethanes as monomers and chain extenders and have traditionally been produced largely from petrochemical sources.[1147] Synthetic routes to biomass-derived diamines have been developed in several instances, and almost exclusively occur *via* biotechnological processes.[1147] This is with the exception of 1,6-hexanediamine, for which extensive research has also occurred *via* chemical, catalytic routes, due to its commercial significance in the production of polyamides.[1148] A recent review by Wang *et al.* discussed in detail the biotechnological pathways to a range of $\alpha,\omega$-aliphatic diamines, although importantly 1,2-ethanediamine was omitted.[1147] While little work on the chemical production of renewable $\alpha,\omega$-diamines exists, the reductive amination of sustainable $\alpha,\omega$-diacids presents an opportunity for the sustainable preparation of a wide range of diamines.

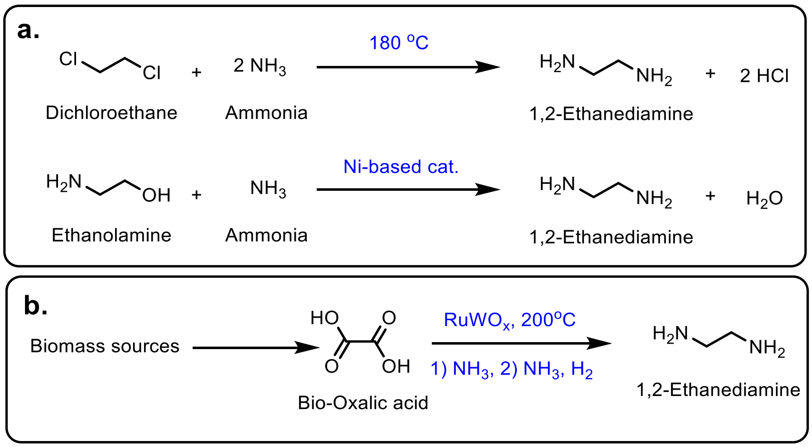


**Figure 92.** (a) Conventional methods for 1,2-ethanediamine (1,2-EDA) production from dichloroethane and ethanolamine, and (b) potential route to bio-based 1,2-EDA *via* the sustainable reductive amination of oxalic acid.

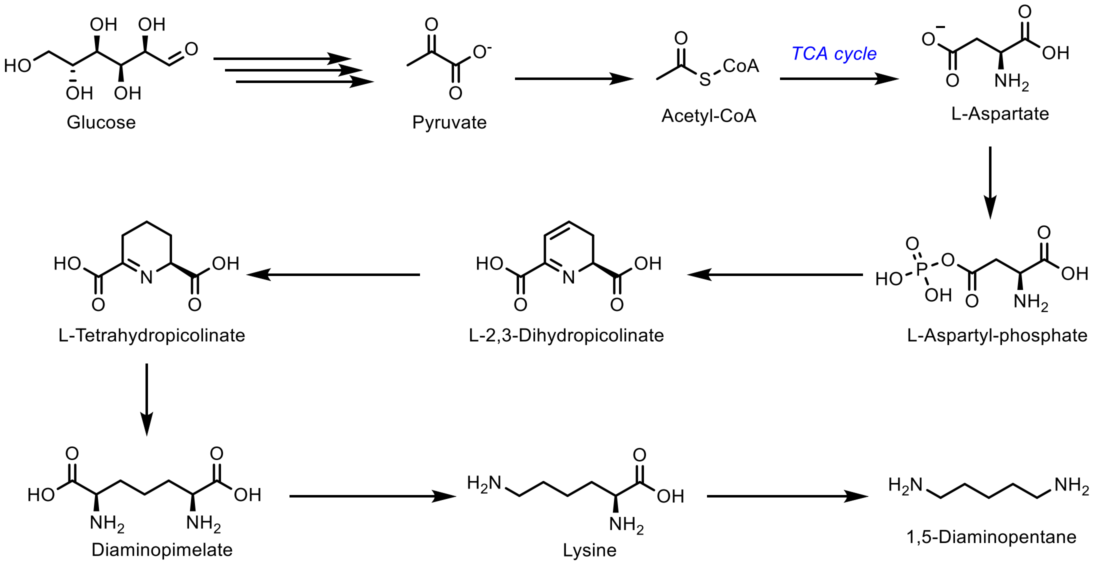


**Figure 93.** Biotechnological production of 1,5-pentanediamine from glucose, *via* L-lysine, where triple arrows indicate multiple steps.

Coeck and De Vos recently published a sustainable one-pot reductive amination of carboxylic acids to primary amines using mild conditions, recyclable heterogeneous $RuWO_x$ catalysts, and achieving yields of up to 96%.[1149] While this has yet to be demonstrated on a significant scale with commercially relevant diamines, it has great potential to be explored as a chemical route to diamine step-growth monomers (Figure 91).

*5.1.3.1. C2 Diamine.* 1,2-Ethanediamine (1,2-EDA, ethylene diamine) has a range of uses, including within polymer synthesis. Industrially, 1,2-EDA is made by the reaction of ammonia with either 1,2-dichloroethane or ethanolamine (Figure 92).[1150,1151] However, in 2012 Metabolic Explorer filed for a patent on the fermentative conversion of L-serine to 1,2-EDA, suggesting commercial interest in a renewable synthesis route.[1152] To the best of our knowledge, there are no published research articles exploring the direct synthesis of 1,2-EDA from sustainable sources, making 1,2-EDA a primary candidate for further research. Due to the numerous routes to bio-based oxalic acid (OA, section 5.1.1), the above-mentioned reductive amination of OA may present a good starting point to develop a sustainable production of 1,2-EDA (Figure).[1149]

*5.1.3.2. C3 Diamine.* 1,3-Propanediamine (1,3-PDA) has a variety of potential uses, including within step-growth polymers, as a cross-linker in epoxy resin systems, or as a pharmaceutical, agrochemical or chemical precursor. Two natural pathways to 1,3-PDA have been investigated, the C4 and C5 pathways in *Acinetobacter baumannii* and *P. aeruginosa*, respectively.[1153−1155] Due to the cosubstrate required in the C5 pathway, the C4 pathway is considered more efficient.[859] An engineered *E. coli* strain produced a titer of 13 g $L^{-1}$ of 1,3-PDA from L-aspartate, highlighting the potential for efficient 1,3-PDA production *via* engineered microorganisms (Table 20, entry 14).[859,1156] However, the L-aspartate substrate limits scalability and future routes from more readily available bioresources such as xylose are necessary.

*5.1.3.3. C4 Diamine.* With potential uses within bio-plastics, surfactants and the agricultural and pharmaceutical industry, demand for 1,4-BDA could rise far past the current demand of approximately 10 kT $annum^{-1}$.[1156,1157] Two routes to 1,4-BDA are found in a wide range of organisms from L-arginine or L-ornithine.[1156] A single-step reaction catalyzed by L-ornithine decarboxylase ODC converts L-ornithine to 1,4-BDA, while L-arginine decarboxylase ODC catalyzes the conversion of L-

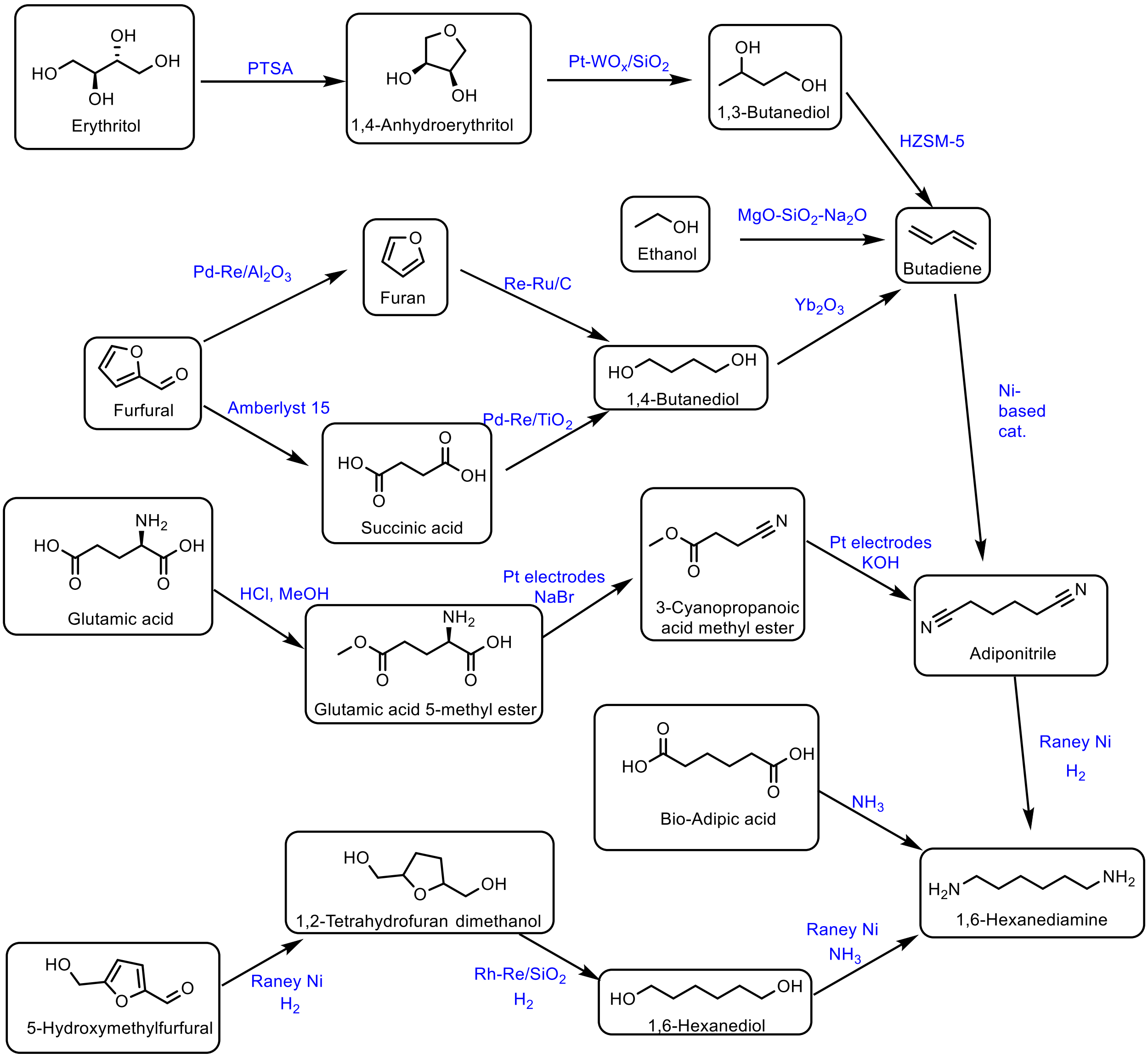


**Figure 94.** Range of routes to 1,6-hexanediamine (1,6-HDA) production from biomass sources.

arginine to agmatine, which is then converted to 1,4-BDA by agmatinase.[1158] Both *E. coli* and *C. glutamicum* have been engineered and optimized to produce 1,4-BDA, with highest reported titers of 42.3 and 19 g $L^{-1}$ of 1,4-BDA from glucose, respectively (Table 20, entry 15).[1156,1158−1162]

*5.1.3.4. C5 Diamine.* 1,5-PeDA, a C5 platform chemical, is currently biosynthesized *via* the decarboxylation of L-lysine, but has also been obtained *via* both whole-cell bio-conversion and direct fermentation processes (Figure 93).[1147] Engineered *E. coli* with overexpressed lysine decarboxylases from various organisms have been developed for the whole cell bioconversion of L-lysine to 1,5-PeDA.[1163−1165] The cell membranes of the impose a mass transfer bottleneck, limiting 1,5-PDA production in whole-cell bioconversion.[1147] Overexpression of the genes responsible for L-lysine intake and 1,5-PeDA secretion resulted in the highest reported 1,5-PeDA titer and yield, 221 g $L^{-1}$ and 92%, from L-lysine (Table 19, entry 16).[861,1166] Whole-cell bioconversion to 1,5-PeDA has been commercialized on an industrial scale by two companies in China, Ningxia EPPEN Biotech (Ningxia) and Cathay Industrial Biotech (Shanghai).[1167]

However, the L-lysine feedstock increases the cost of whole-cell bioconversion, relative to the cost of cheaper, more abundant, sugar feedstocks. Direct fermentation of sugar feedstocks to 1,5-PeDA is highly desirable for the future of sustainable 1,5-PeDA production and has been investigated with *E. coli* and *C. glutamicum* as engineered host microbes. Despite not naturally producing detectable amounts of 1,5-PeDA, *E. coli* was engineered with suppressed 1,5-PeDA degradation and overexpressed 1,5-PeDA production.[1168,1169] An additional iteration of relevant gene suppression gave a titer of 12.6 g $L^{-1}$ of 1,5-PeDA from a glucose-containing medium.[1170] *C. glutamicum* has naturally high L-lysine production and has potential for the direct fermentation of glucose to 1,5-PeDA if L-lysine can be produced as an *in situ* feedstock for 1,5-PeDA production (Figure 93).[1147] Engineered *C. glutamicum* strains have reached 1,5-PeDA titers of 103.8 g $L^{-1}$ (Table 19, entry 17).[862,1171−1173] To decrease production costs and avoid conflicting with food supplies, a different engineered *C. glutamicum* strain reached a 1,5-PeDA titer of 103 g $L^{-1}$ from xylose, almost as high as the titer from glucose (Table 19, entry 18).[863,1174] Methanol, produced on a

**Table 21. Catalysts, Conditions and Yields for the Chemical Production of 1,6-Hexanediamine and Its Intermediates from Biomass Sources *via* Chemical Conversion**

| Entry | Target | Feedstock | Catalyst | Temperature (°C) | Pressure (bar) | Conversion (%) | Selectivity (%) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Butadiene | Ethanol | MgO-$SiO_2$-$Na_2O$ | 350 | 1 ($N_2$) | 100 | 87 | 87 | 1196 |
| 2 | Butadiene | Furfural | 1) Pd-K/$Al_2O_3$<br>2) Re-Ru/C<br>3) $Yb_2O_3$ | 1) 260<br>2) 160<br>3) 360 | 1) nr<br>2) 30 ($H_2$)<br>3) 1 ($N_2$) | nr | nr | 66 | 1) 1206<br>2) 1210<br>3) 1211 |
| 3 | Butadiene | Furfural | 1) Amberlyst-15<br>2) Pd-Re/$TiO_2$<br>3) $Yb_2O_3$ | 1) 80<br>2) 160<br>3) 360 | 1) nr<br>2) 150 ($H_2$)<br>3) 1 ($N_2$) | nr | nr | 59 | 1) 590<br>2) 572<br>3) 1211 |
| 4 | Butadiene | Erythritol | 1) Ion-exchange resin<br>2) Pt-$WO_x$/$SiO_2$<br>3) $SiO_2$/$Al_2O_3$ | 1) nr<br>2) 140<br>3) 300 | 1) nr<br>2) 80 ($H_2$)<br>3) 1 (nr) | nr | nr | 29 | 1) 1212<br>2) 1214<br>3) 1215 |
| 5 | Adiponitrile | Butadiene | Ni(acac)$_2$/Xantphos | 150 | 1 (Ar) | nr | nr | 28 | 1193 |
| 6 | Adiponitrile | Me-GluAc | Pt electrodes | 1) 0<br>2) 60 | nr | nr | nr | 61 | 1216 |
| 7 | 1,6-HDA | Adiponitrile | Raney Ni 2400 | 100 | 30 ($H_2$) | 100 | 100 | 100 | 1187 |
| 8 | 1,6-HDA | Adiponitrile | PdAg | 50 | nr | 99 | 99 | 98 | 1217 |
| 9 | 1,6-HDA | 5-HMF | 1) Raney Ni<br>2) Rh-Re/$SiO_2$ + Nafion SAC-13<br>3) Raney Ni | 1) 100<br>2) 120<br>3) 200 | 1) 90 ($H_2$)<br>2) 10 ($H_2$)<br>3) 138 (nr) | nr | nr | 34 | 1) 549<br>2) 549<br>3) 1218 |

60 MT annum$^{-1}$ scale and available from biomass, has been used as a cosubstrate for 1,5-PeDA by an engineered *C. glutamicum* strain, presenting an additional potential secondary feedstock for 1,5-PeDA production.[1175−1179]

*5.1.3.5. C6 Diamine.* 1,6-Hexanediamine (1,6-HDA), commonly known as hexamethylenediamine, is in huge demand as a monomer for the synthesis of polyamides 66 and 610, with the former responsible for ∼50% of all polyamides currently produced.[1148] Almost all routes to 1,6-HDA are chemo-catalytic in nature, although a multi-step bioconversion of 2-amino-6-oxopimelate has been developed, and several non-natural metabolic pathways to 1,6-HDA have been proposed[1004,1147,1180] 1,6-HDA is synthesized by hydrogenation of adiponitrile, *via* 6-aminocapronitrile, at high temperatures by a range of metal catalysts.[1181−1189] 1,6-HDA is not yet produced from biomass on an industrial scale due to economic and technical limitations when compared to traditional petrochemical adiponitrile sources.[1148] Due to the high purity requirements for use in nylon-66 synthesis and the difficulties removal of homogenous catalysts, particular focus has been given to the development of heterogeneous catalysts.[1148,1190,1191]

The simplest route to bio-based 1,6-HDA is to produce renewable adiponitrile for use as a drop-in substitute in 1,6-HDA synthesis. Adiponitrile is most often made *via* the hydrocyanation of butadiene, which can be generated from a number of biomass derivatives such as ethanol, furfural, and 1,4-anhydroerythritol (Figure 94).[1148] Butadiene hydrocyanation is conducted by Du Pont with a Ni-based catalyst and HCN in two steps, but a more sustainable system utilizing formamide to provide a cyano group without the need for HCN has been developed by Shu *et al.*, albeit with only 28% yield.[1192,1193] Bio-ethanol can be converted to butadiene in a single step *via* the Lebedev process (Figure 94, Table 21, entry 1).[1194−1200] Furfural, produced on a 0.5 MT scale yearly from hemicellulose, provides two distinct routes to 1,6-HDA *via* 1,4-butanediol (1,4-BDO) (Figure 94, Table 21, entries 2 and 3).[1201−1203]

Furfural can be oxidized to SA and then hydrogenated to 1,4-BDO, or decarbonylated to furan and then converted to 1,4-BDO using a bimetallic catalyst.[571,573,590,820,1204−1210] The best reported overall 1,4-BDO yields of these two routes are 61% and 68%, respectively, although both utilize catalysts containing palladium, an expensive rare earth metal.[573,843,1148,1206,1210] 1,4-BDO is then dehydrated to butadiene, which has been reported with a yield of 97% using additional rare earth oxide catalysts.[1211]

Erythritol, produced from biomass on a 60 kT scale annually, can also be converted into butadiene (Figure 94, Table 21, entry 4). It is first dehydrated to 1,4-anhydroerythritol by simple Brønsted acid catalysts, with yields that can exceed 90% if reactive distillation systems are utilized.[1212,1213] Then, hydrogenolysis of 1,4-anhydroerythritol with a Pt- and W-containing catalyst produces 1,3-BDO with a yield of 54%.[1214] Finally, the 1,3-BDO is dehydrated to butadiene with a 60% yield using a zeolite catalyst, although catalyst deactivation occurs shortly after 100 h of use.[1215] Both 1,3-BDO and 1,4-BDO can be produced *via* biotechnological routes (section 5.1.2), and these could be integrated with the mentioned butadiene syntheses. The butadiene obtained *via* all the routes can then be converted into adiponitrile though multi-stage hydrocyanation (Table 21, entry 5).

Adipic acid (AA) was formerly the dominant route to adiponitrile *via* high-temperature ammonization, although it is no longer used on a large scale due to economic reasons.[1219,1220] If AA can be obtained from biomass (section 5.1.1.4), this would provide an additional route to bio-based 1,6-HDA. An electrochemical synthesis of adiponitrile from glutamic acid 5-methyl ester (Me-GluAc) *via* 3-cyanopropanoic acid methyl ester has been reported with Pt-containing electrodes.[1216] Me-GluAc is easily accessible at high yields from glutamic acid (GluAc), and the combined steps from GluAc to adiponitrile have a yield of 58% (Table 21, entry 6).[1148,1221] Electrochemical processes are considered more environmentally friendly than traditional chemical synthesis due to the potential use of renewable energy sources instead of harsh chemicals.[1222] A series of hydrogenation steps converts

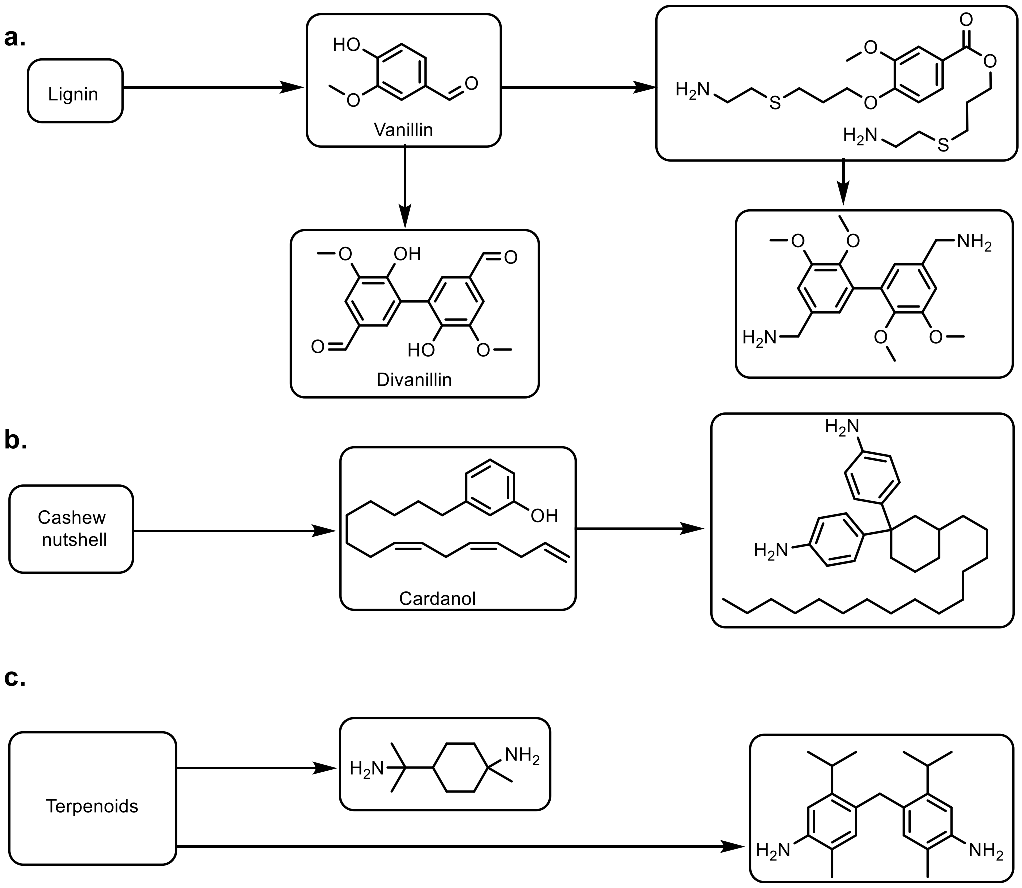


**Figure 95.** Examples of aromatic/cyclic aliphatic diamines produced from three key bio-based sources, i.e., (a) lignin, (b) cashew nutshell and (c) terpenoids.

adiponitrile to 1,6-HDA, although there are several possible side-products that can reduce yields and introduce impurities, and these must be minimized.[1223,1224] Several techniques to impede side-product formation and increase 1,6-HDA yields have been reported, including the addition of ammonia, water, alkali metal hydroxides and ionic liquids, and the highest yields have been obtained with Raney catalysts.[1187,1225−1228] For instance, Raney Ni has been used to achieve a quantitative yield of 1,6-HDA from adiponitrile with $H_2$ at 100 °C (Table 21, entry 7).[1187] However, using molecular $H_2$ in the hydrogenation steps can be considered less sustainable due to its common production from petrochemicals, and the hazards associated with using $H_2$ at high pressures (~3 MPa).[1229] Alternatively, formic acid, which can be sustainably produced, was used as a hydrogen donor for the hydrogenation of adiponitrile with Pd−Ag nanowires, with a 1,6-HDA yield of 98% achieved (Table 21, entry 8).[1217]

Bypassing adiponitrile, 1,6-HDA can also be made from 5-hydroxymethylfurfural (5-HMF), a platform chemical produced from glucose *via* isomerization to fructose and subsequent dehydration (Table 21, entry 9).[1230−1233] 5-HMF is hydrogenated with Raney Ni to 2,5-tetrahydrofurandimethanol, hydrogenated again to 1,6-hexanediol (1,6-HDO), and then aminated to 1,6-HDA.[1129,1218,1234,1235] The first two steps have a high combined yield of 85%, but the final amination step has a low yield of 40%.

Widespread adoption of non-petrochemical routes to 1,6-HDA is impeded by the prices of necessary intermediate chemicals, and the repurposing of waste materials from these routes could generate additional value, such as use as fuel for energy generation.[1236] The 5-HMF route to bio-derived 1,6-HDA is considered the most competitive, with the prices of petrochemical and corn-syrup-derived 1,6-HDA estimated at \$1.84 and \$2 $kg^{-1}$, respectively.[1237] While the petroleum route narrowly remains the cheapest route, optimization of the final amination step, increasing butadiene prices, or decreasing corn syrup prices would shift the economic choice toward bio-based 1,6-HDA.[1237] Life cycle assessment of the 5-HMF bio-based route to 1,6-HDA established that the process acts as a carbon sink, presenting an advantage when considering the climate, but can also have a higher impact on the environment, terrestrial and marine ecosystems and freshwater eutrophication.[1237]

*5.1.3.6. Long-Chain Diamines.* Engineered *E. coli* have been designed to express an alanine dehydrogenase, which can produce non-natural diamines from their corresponding diols, L-alanine and ammonium chloride.[1238] 1,8-Diaminoactane, 1,10-diaminodecane and 1,12-diaminododecane were produced with yields of 87%, 100% and 60%, respectively. A similar system with *E. coli* expressing an aldehyde reductase and a transaminase yielded the same three diamines with yield of 96%, 57% and 39%, respectively.[1239] No direct metabolic pathway from biomass sources to long-chain diamines has been reported, but chemical conversion of biomass could be used to produce long-chain diamines, such as *via* the amination of castor oil-derived sebacic acid.[1240] Croda produce a diacid from dimerizing unsaturated fatty acids, which has been converted to diamine and commercialized under the brand name Priamine (Figure 78c).[1241] The nature of the dimers is the same as those previously mentioned (Section 5.1.1.5), only with the diacid functionality replaced with diamine functionality.

*5.1.3.7. Aromatic Diamines.* Aromatic diamines are key building blocks in the chemical industry, and the development of aromatic diamines from renewable carbons opens the possibility for a range of novel bio-based polymers with useful properties such as high strength and high melting and glass transition temperatures.[1147] In recent years, bio-based diamines have been derived from three key biomass feedstocks: lignin, cashew nutshell and terpenoids, with some examples shown in Figure 95.

Lignin, as the most abundant source of aromatics from biomass, is the ideal feedstock for aromatic bio-based diamines. Vanillin is produced commercially from lignin and can be converted to pure divanillin *via* enzymatic catalysis (Figure 95a).[1242−1244] Three diamines have been derived directly from vanillin, while two more have been derived from divanillin, with the resultant diamines containing multiple pendant methoxy groups and one or two aromatic rings, respectively.[1244,1245] The latter have been used to cross-link bio-based epoxy thermosets, exhibiting utility within thermoset materials.[1246]

Cashew nutshell liquid is an attractive biomass feedstock due to its low cost, high abundance, and easy separation into various valuable chemicals exhibiting unique structural features.[1247,1248] An excellent review article on the synthesis of bio-based amines had been reported by Caillol et al.[1248] One such chemical, isolated *via* distillation, is cardanol, which contains an unsaturated alkenyl side chain, an aromatic ring and a phenolic hydroxyl group, and is considered desirable for the synthesis of difunctional monomers (Figure 95b).[1247,1248] Multiple diamines have been derived from cardanol, with diverse structural features such as long aliphatic spacers or the removal of the phenyl hydroxyl functionality.[1249−1251]

Terpenoids are abundant biomass hydrocarbon compounds have also been shown as a potential source of a range of diverse bio-based aromatic compounds. A primary non-aromatic aliphatic cyclic diamine, menthane diamine, was synthesized at low temperature in the presence of water, sulfuric acid and hydrogen cyanide, while *p*-cymene was converted to a diamine containing two aromatic rings (Figure 95c).[1239,1252]

### 5.1.4. Diisocyanates.

Diisocyanates are most commonly combined with polyols in the synthesis of polyurethanes, a prominent class of polymers discovered 70 years ago.[1253] The most commonly used diisocyanates are the aromatic methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), as well as hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), constituting 61%, 34%, 3.4% and 1.2% of global demand, respectively (Figure 96a).[1254] There are several serious concerns with conventional isocyanate synthesis, including non-renewable petrochemical feedstocks, the use of toxic reactants and the toxic nature of the isocyanates themselves.[1253] The replacement of conventional diisocyanates with bio-based drop-in analogues presents the most likely shift toward more sustainable polyurethanes and polyureas, particularly in the short term. Non-isocyanate routes to polyurethanes and polyureas offer more sustainable long-term routes and are discussed later (sections 5.2.3 and 5.2.4, respectively).

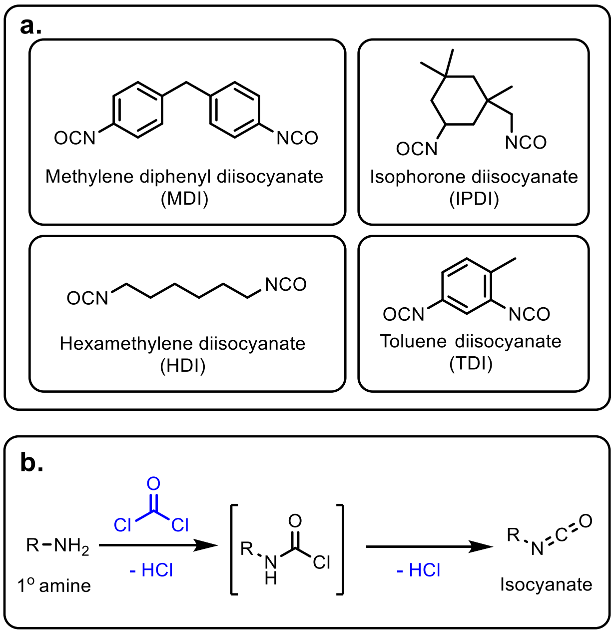


**Figure 96.** (a) Four most common diisocyanates, and (b) conventional synthetic route to isocyanates.

Conventional diisocyanates are synthesized through a number of different routes, the most commonly being the reaction of primary amines with phosgene (Figure 96b).[1253] Although efficient, avoiding the direct use of extremely toxic phosgene gas is highly desirable, and several phosgene derivatives such as trichloromethyl chloroformate and bis(trichloromethyl) carbonate are often used at a lab scale.[1253] Other, safer, methods include the application of stoichiometric amounts of di-*tert*-butyl dicarbonate ($Boc_2O$), the nucleophilic substitution of alkyl halogenides, triflates, tosylates or mesylates with metal cyanates, the thermal decomposition of carbamates, and the use of triphenylphospine, 2,3-dichloro-5,6-cyanate and tetrabutylammonium cyanate to trimethylsilyl ethers, alcohols and thiols.[1255−1258] On a lab scale, additional frequently used methods utilize hazardous chemicals such as azides, $Br_2$, acetyl chloride and ammonium persulfate.[1253,1258]

There are several routes to diisocyanates that are considered more sustainable than conventional isocyanate synthesis methods. For example, aryl isocyanates such as TDI and MDI can be obtained *via* the reductive carbonylation of nitroarenes with carbon monoxide.[1259,1260] A range of catalysts based on metals, including Te, Se, S and a range of group 8−10 metals have been successfully used in these reactions, but catalyst residues in products commercialization *via* this method.[1253,1260] More commonly used is the carbonylation to *N*-phenyl carbamates, followed by a thermal decomposition to isocyanates, for which many catalysts have been described, including cheap iron-based catalysts.[1261−1264]

The conversion of isocyanides also presents a possible route to isocyanates, with a sustainable oxidation procedure applying DMSO and catalytic amounts of trifluoroacetic anhydride described by Le and Ganam, where earlier methods often utilized hazardous oxidation agents containing mercury or lead.[1265] Isocyanides are commonly made by the dehydration of *N*-formamides, which can be readily prepared in a sustainable manner from primary amines *via* heating in recyclable formic acid or formic acid esters (Figure 97).[1266] The dehydration step presents a barrier to sustainability, but a recent paper by Meier and colleagues developed a sustainable dehydration process using *p*-toluenesulfonyl chloride (*p*-TsCl)

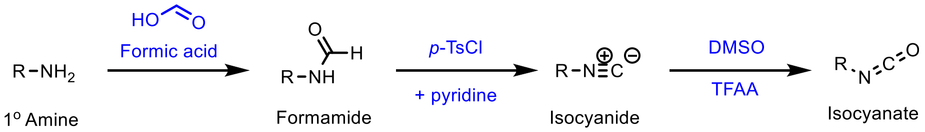


**Figure 97.** Procedure for the conversion of a primary amine to an isocyanate, *via* an isocyanide intermediate.

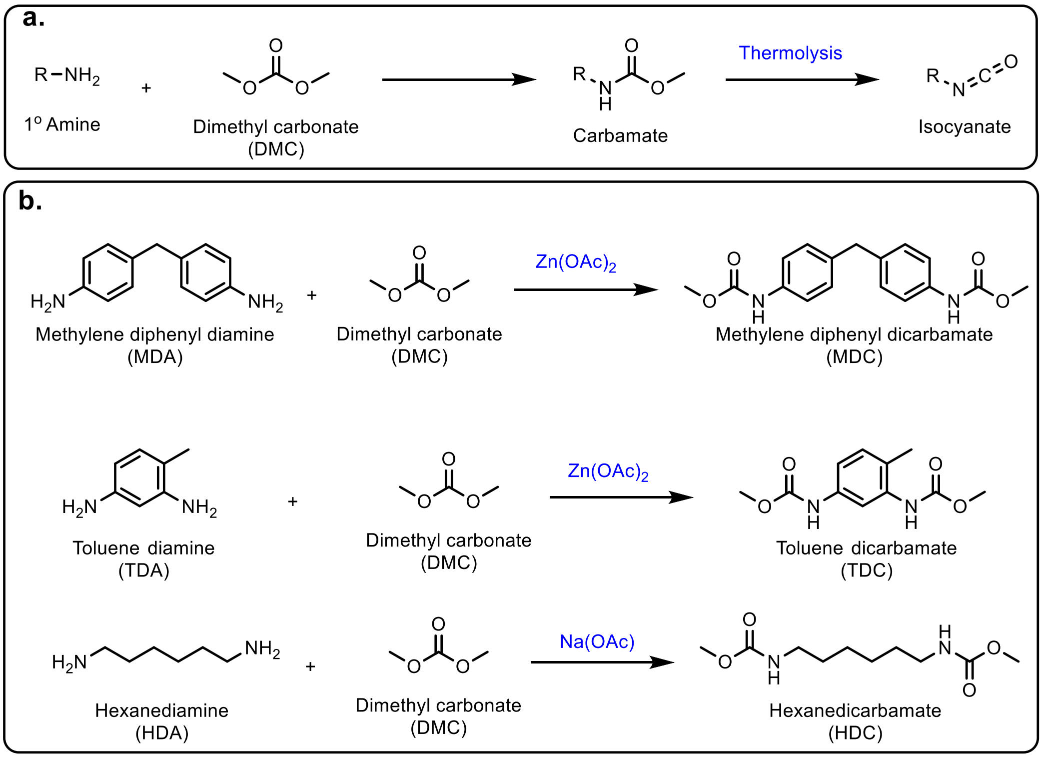


**Figure 98.** (a) General scheme for the synthesis of an isocyanate from a primary amine and dimethyl carbonate, *via* a methyl carbamate intermediate, and (b) established syntheses of the dimethyl carbamate precursors to three commonly used diisocyanates.

and pyridine.[1267] Notably, *p*-TsCl can be obtained as an industrial waste product and is readily available, while pyridine reportedly presents the least hazardous option when compared to many other common amines.[1267] Hence, the combination of bio-based diamines with sustainable conversion processes to *N*-formamide, isocyanide, and finally isocyanate, presents one attractive route to sustainable, bio-based diisocyanates. However, while more sustainable than the preceding routes, these processes still require solvents such as DMSO and stoichiometric amounts of base.

Carbamates, also known as urethanes, are key intermediates in isocyanate synthesis, and can also be directly converted to polyurethanes *via* transesterification with a diol, bypassing the need for diisocyanates.[1253] Previously, silanes and boron halogenides were used as catalysts, limiting the reaction scale due to toxicity and high prices, and aliphatic carbamates were avoided due to side reactions in the thermal fragmentation.[1258,1268] Recently, the conversion of carbamates to isocyanates *via* thermal decomposition was modelled, although this focused on the preparation of mono-isocyanates, and the authors note that many industrial patents exist concerning this process, suggesting companies have calculated the process to be commercially viable.[1269] Carbamates have traditionally been produced from alcohols and amines with phosgene derivatives, such as chloroformates, which is suitable for lab-scale peptide chemistry but not appropriate for large-scale synthesis.[1259] Three well-known rearrangements enable carbamate production from carboxylic acids; the Curtius rearrangement of acyl azides, the Lossen rearrangement of hydroxamic acids and the Hoffman rearrangement of carboxamides.[1253,1259] However, these pathways suffer from toxic and often explosive reagents, which could limit the processes' scalability and sustainability.[1270,1271] Modern Hoffman procedures have enabled the conversion of amides to methyl carbamates with hypervalent iodine under mild conditions.[1272] As well as from amines, alcohols, and acid derivatives, routes from nitriles, aldehydes and ketones to carbamates exist, but these also suffer from sustainability issues.[1259]

In recent years, more sustainable routes to carbamates have emerged, with the conversion of organic carbonates appearing the most promising.[1253] The catalytic conversion of primary and secondary amines with dialkyl/diaryl carbonates, first reported in 1983 with *N*,*N*′-disuccinimido carbonate, has since been reported with a number of activated carbonates.[1253,1273,1274] More recently, catalysts systems such as $Zr(Ot\text{-}Bu)_4$/1-hydroxypyridine have been reported for the conversion of amines using non-activated dialkyl carbonates.[1275] The dimethyl carbamate precursors of TDI and MDI, the most industrially relevant diisocyanates, were prepared with almost-quantitative yields from their corresponding aniline and dimethyl carbonate (DMC) with 1.0 mol % zinc acetate as a catalyst (Figure 98b).[1276] Similarly, sodium acetate has been shown as an effective catalyst for the conversion of 1,6-hexanediamine (HDA) and DMC *via*

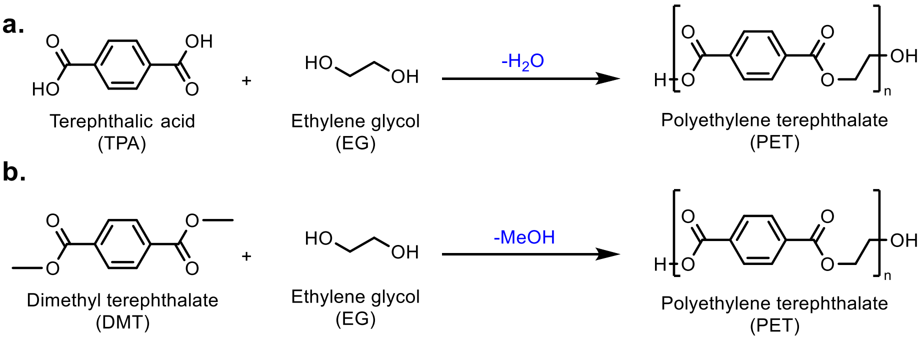


**Figure 99.** Production of polyethylene terephthalate *via* (a) polyesterification of TPA and EG, and (b) transesterification of DMT and EG.

methoxycarbonylation.[1277] A strong guanidine base, 1,5,7-triazobicyclo [4.4.0]dec-5-ene (TBD), catalyzes carbamate formation from DMC with primary, renewable diamines, as well as from DMC with primary, secondary and tertiary diols, although a number of other catalysts have been reported.[1278−1280]

Enzymatic alkoxycarbonylation has been used to achieve chiral carbamates, mono-substitution of a diaminonucleoside and other interesting carbamates.[1253,1281,1282] Catalyst-free synthesis of methyl carbamates from aliphatic amines and dimethyl carbonate was achieved in 2005 in supercritical $CO_2$ at 130 °C, with yields reaching 90% within 4 h.[1283] Meier and co-workers introduced an eco-friendly synthesis of carbamates from hydroxamic acids *via* the aforementioned Lossen rearrangement with a range of dialkyl and diaryl carbonates.[1284] Using a recyclable solvent mixture with catalytic amounts of tertiary amine bases, anilines were produced with yields of up to 83%, presenting a promising process for the synthesis of carbamates from carboxylic acids. Other routes to carbamates with potentially sustainable credentials include a three-component reaction of a primary or secondary amine with $CO_2$ and an electrophile, sustainable oxidation of aromatic aldehydes with urea hydrogen peroxide, and Cu-catalyzed oxidative C−O coupling of fully substituted formamides.[1259,1285−1287] The latter is particularly promising due to the simple access to formamides from the reaction of the corresponding amine with sustainable formic acid.[1266]

To use organic carbonates for the synthesis of sustainable carbamates, the carbonates themselves must be sustainably produced. There are well-known procedures for the synthesis of DMC that do not require phosgene or derivatives thereof.[1288] These are the catalytic conversion of $CO_2$ and MeOH, the catalytic oxidative carbonylation of MeOH, the catalytic conversion of urea, and the two step conversion of ethylene/propylene oxide with $CO_2$. The first route produces water that must be removed to drive the reaction equilibrium, which has been circumvented in several ways.[1289−1291] Catalysts such as $CeO_2$ and KCl-doped-$ZrO_2$ have been used, but an ionic-liquid-supported $Ce_xZr_{1-x}O_2$ catalyst proved the most promising catalyst system, although others have been described.[1292,1293] A number of methods have been developed for the oxidative carbonylation of methanol to DMC, with an efficient and recyclable Schiff base/zeolite catalyst developed by Li and co-workers.[1294−1296] A series of zinc based catalysts have been applied for the conversion of urea to DMC with an alcohol, and a selective batch-fed urea methanolysis system using an $Fe_2O_3$-based catalyst has also been reported.[1297−1300] The most common method for the preparation of carbonates is a conversion of ethylene/propylene to ethylene/propylene oxide and its subsequent transesterification with MeOH to give DMC.[1253] A range of catalysts including Mg-, Au- and phosphonium halide-based systems, a KI/$K_2CO_3$ mixed system, and an electrochemical ionic liquid system have been explored for this route.[1253,1301−1307] As evidenced by the above examples, and the additional unmentioned routes to DMC, DMC appears to be a readily available nontoxic phosgene substitute for the synthesis of carbamates, and hence diisocyanates and their polyurethane and polyurea derivatives.

## 5.2. Step-Growth Polymers

Unlike the other sections of this review, the difunctional monomers mentioned within this section must be combined with a second difunctional monomer to give an AA+BB step growth polymer. Hence, having discussed the most important monomers within each class, it is important to frame the significance of the monomers by briefly discussing the 5 relevant polymer classes. While the overall focus of this review is on producing the monomers already commonly used, this section will also highlight areas where common polymers may be displaced by alternative polymers in the future, as well as polymers that may have great potential but are currently underutilized.

**5.2.1. Polyesters.** Polyester materials are incredibly important polymer materials that contain an ester bond within their repeat unit and find wide-ranging applications in plastic bottles, films and textiles. Although technically comprising of a whole class of polymers, the term polyester is used ubiquitously to refer to polyethylene terephthalate (PET), which currently dominates the polyester market. Indeed, in 2020, the global PET annual production was over 57 million tons with a market size of approximately $110 billion.[1308]

The largest applications of PET are in fibers for textile production (60%) and bottles for water and carbonated drinks (30%). PET possesses several attractive properties for these applications, such as high hardness, stiffness and strength, a wide service range, controllable transparency and high hydrolytic resistance at room temperature. PET is produced from ethylene glycol (EG) and either terephthalic acid (TPA) or its dimethyl terephthalate (DMT) derivative in a (trans)-esterification polymerization reaction (Figure 99). Conventionally, all these monomers were obtained from petrochemical sources, but in recent decades routes have emerged to produce EG, TPA and DMT from biomass sources. The bio-based production of EG is far more developed than that of TPA, due to the aromatic structure of TPA being more cumbersome to derive from readily available bio-based feedstocks. Moreover, bio-ethanol production is well-established as a main EG feedstock. As such, the earliest instances of incorporating biomass into PET production combined bio-derived EG with petrochemically sourced TPA or DMT, as demonstrated in 2009 when Coca Cola introduced a bottle containing 30% biomass.[1309]

Since then, fully bio-based PET has been demonstrated in fiber applications and commercialized in soft-drinks bottle applications *via* the inclusion of TPA derived from bio-based *p*-xylene.[986,987] However, the scale of these operations are tiny relative to overall PET production, and is far from presenting a solution to the needs for PET supply. While mainly outside the scope of this review, it is worth mentioning that large effort in recent decades has been invested in developing the technology to recycle PET, either mechanically or chemically, with companies aiming to include 50% recycled PET in their products by 2030.[1310,1311] Hence, any sustainable future for the use of PET would rely on a combination of continuing to move away from petrochemical feedstocks and further developing PET recycling technology, hence reducing the demand for virgin petrochemically sourced PET.

Aside from PET, a range of other polyesters have been shown to have great commercial potential, even outperforming PET in specific applications. These include poly(lactic acid) (PLA), poly(butylene succinate) (PBS) and poly(ethylene 2,5-furanoate) (PEF), among several others.[1312−1314] PLA, produced *via* ring-opening polymerization of lactides (cf. section 4.3), is a widely used bio-based plastic with impressive physical properties but weaker thermomechanical properties than PET.[1312,1313] PBS, an aliphatic polyester produced from 1,4-butanediol (1,4-BDO) and succinic acid (SA) in a polycondensation process similar to that of PET, exhibits promising sustainability due to its production from sustainable feedstocks and its biodegradability.[1315] Both SA and 1,4-BDO have established production routes from biomass, with more continuing to be developed, as has been discussed in previous sections. Additionally, the degradable nature of ester linkages combined with the small metabolism-compatible aliphatic degradation products, give PBS biodegradable properties. In soil, PBS degrades significantly faster than conventional plastics, with numerous microorganisms documented to assist in its degradation.[1315] PBS benefits from rigidity and transparency, and has found applications within compostable tableware, food packaging and agricultural mulch films, as well as various biomedical applications.[1316−1319] However, PBS use is currently limited by its relatively high price at ∼\$50 $kg^{-1}$, being an order of magnitude greater than that of PET.[1315] As PBS production grows, this price differential can be predicted to shrink, although the incredibly cheap nature of petrochemically sourced PET means that PBS will still remain substantially more expensive for the foreseeable future.

PEF is considered a top candidate for the phasing out of petrochemically sourced polyesters such as PET, in particular due to furan-2,5-dicarboxylic acid's (FDCA) position as an aromatic bio-based platform chemical and PEF's thermomechanical properties resembling those of PET (Figure 100).[995,1320−1322] As with most AA+BB type polyesters, PEF synthesis follows similar routes to those described for PET production, and Fei *et al.* recently reviewed a range of polyesters derived from FDCA, including PEF.[1312] Since the main issue with PET production is sourcing TPA, PEF provides an alternative, where the same simple diol and a similar aromatic diacid are used. Furthermore, food-contact-grade PEF has been produced with low discoloration and high transparency, and PEF has been demonstrated to possess $O_2$ and $CO_2$ barriers 10-20 times than those of PET, and water barriers twice as great.[1323−1325] This has been attributed to the nonlinearity of the furan structure in FDCA inhibiting ring-flipping.[1326] Avantium have a test plant in the Netherlands producing FDCA and then PEF using their melt-polymerization YXY® Technology, and plan to produce 5 kT $annum^{-1}$ in a pilot plant opening in 2023.[1327,1328] Additionally, researchers at ETH Zürich have produced bottle-grade PEF from cyclic oligomers, and are working toward adapting them for industrial scale demands.[1329,1330] As PEF is commercialized and more thoroughly investigated, the cost of FDCA will decrease, and the range of applications in which PEF could be beneficially used will become more apparent.

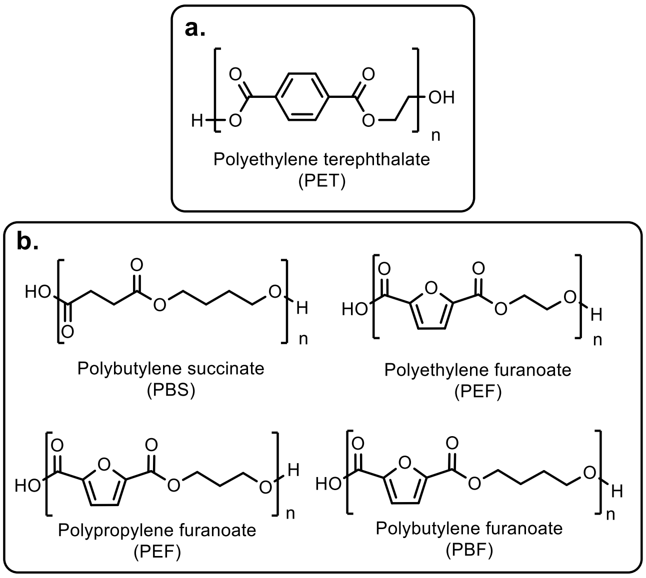


**Figure 100.** (a) Dominant polyester PET, and (b) some promising bio-based polyesters to displace PET in certain applications.

Polybutylene terephthalate (PBT) and polypropylene terephthalate (PPT) are well known engineering plastics made from the reaction of terephthalic acid with 1,4-BDO or 1,3-PDO, respectively.[1312] The FDCA analogues of these polyesters, poly(butylene 2,5-furanoate) (PBF) and poly(propylene 2,5-furanoate) (PPF), have been reported to exhibit comparable thermomechanical properties, in particular thermal stability and mechanical strength, presenting opportunities to reduce the amount of petrochemical TPA required.[1331] Polyesters of FDCA with aliphatic diols (C3−C18) showed glass transition temperatures ($T_g$) decreasing from 90 °C in PPF to under 0°C in poly(dodecyl 2,5-furanoate), enabling a range of control over thermal properties by diol monomer choice.[1322,1332] Polyesters of FDCA with rigid diols have increased $T_g$ values, as high as 180 °C in the case of poly(isosorbide 2,5-furanoate).[1320] The inclusion of isosorbide in fully bio-based polyesters based on FDCA and short aliphatic diols for food packaging applications increased the $T_g$ by 40 °C, and elsewhere isosorbide content has been shown to increase hydrolytic degradability.[1333,1334]

One of the great benefits of AA+BB polyester synthesis, and AA+BB polymers more generally, is the simplicity of the polymerization processes and the tuneability of the monomer composition to achieve copolymers with a range of desired properties. As the field of polyester chemistry moves away from being a monolith primarily utilizing PET for most applications and the sustainable synthesis of a range of bio-based

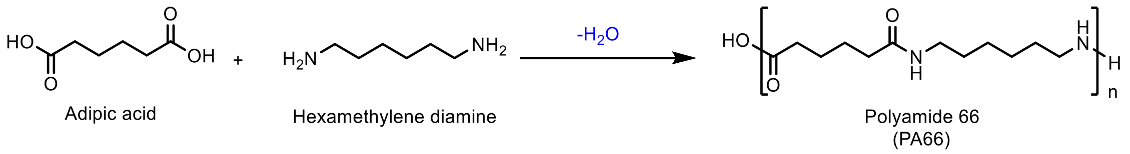


**Figure 101.** Production of polyamide 66 (PA66) from adipic acid and hexamethylene diamine.

difunctional monomers becomes more realistic, a more diverse range of polyesters, including some not described here, will be designed for usage in specific applications. An important consideration for AA+BB polymerizations, however, is the need for precise stoichiometric ratios in order to reach high molecular weights, which can pose demands on reliable bio-based monomer purity and hence could require intensive and costly purification processes.

### 5.2.2. Polyamides.

Polyamide materials, commonly referred to as nylons, are another important class of step-growth polymers that contain an amide bond within their polymeric repeat unit. Polyamides are synthesized from a diamine and a diacid, or derivatives thereof (e.g., acid chlorides, ester). Polyamides find use in a range of applications within the automotive, food, construction, and apparel industries, as well as in many other applications.[860,1169,1335] Nylon-66 (PA66) and nylon-6 (PA6) are the two most commonplace polyamides, with an estimated combined demand of over 1 Mt in 2019 (Figure 101).[1336] Although PA6 is produced by the ring-opening polymerization of caprolactam (cf. section 4.2.2), PA66 can be produced *via* the polycondensation reaction of adipic acid and 1,6-hexanediamine, two monomers that have been explored in detail within this section. The impressive mechanical properties of PA66, including rigidity, high mechanical strength and robustness against heat and chemicals, have cemented its position as a high-performance commodity polymer.[1337] In 2013, Rennovia launched a 100% bio-based PA66 product, but this was discontinued, with Rennovia ceasing operations in 2018.[1338,1339] A recent collaboration between Genomatica and Asahi Kasei seeks to commercialize bio-based PA66.[1340] As bio-based routes to the HDA and AA monomers continue to be developed, PA66 production will likely shift toward bio-based feedstocks. Due to their similar structures and properties, and the lower cost of PA6 over PA66, industries have somewhat prioritized employing PA6 wherever possible.[1341] However, other polyamides with similar properties, which have previously been neglected due to more expensive petrochemical monomer syntheses, may become more commonly used if they can be produced from biomass sources more easily than the PA66 monomers.

Besides HDA, the most promising diamine for bio-based commercialization is 1,5-PeDA, which can be copolymerized with AA to give PA56. PA56 is regarded as the bio-based polyamide best-suited to displace PA66, due to their similar structures and the potential for high-volume 1,5-PeDA production.[1342] While PA56 underperforms in some ways, such as being brittle at low-temperatures and having poor notched impact strength, blending with an elastomeric interfacial compatibilizer has had an ultra-toughening effect on PA56.[1342] As such, PA56 may replace PA66 in some applications if and when it is commercialized. Other polyamides, such as PA610 and P612, produced from the copolymerization of HDA with sebacic acid (C10) and dodecanedioic acid (C12), respectively, can also be produced from bio-sourced monomers, and exhibit lower moisture absorption and heat resistance than PA56.[1342−1345] However, the production of these diacid monomers from bio-sources is still under-developed.

Of the discussed aliphatic diacids, oxalic acid (C2) and succinic acid (C4) appear the most promising for large-scale bio-based production, and these can be copolymerized with 1,5-PeDa to give PA52 and PA54, respectively. PA52, first prepared by Mutua *et al.* in 2018, has the shortest possible diacid component and exhibits high heat-resistance, low water absorption, and excellent crystallizability.[1346] With thermal stability equal to that of PA6, PA52 is very appealing as a bio-based high performance engineering plastic. PA54, first prepared by Lee *et al.* in 2020, has not been the subject of much work, although one study investigated the formation of the nylon salt of the two monomers. In another report, direct solid-state polymerization was employed in place of melt-polymerization, due to the tendency of SA to undergo intra-cyclisation at high temperatures.[1347−1349] Although the synthesized PA54 degraded at temperatures lower than conventional polyamides (i.e., 320 °C), the melting point remains higher than that of PA66 (i.e., 275 °C).[1347,1349] Due to its higher amide group concentration, PA54 possessed higher water absorption than PA66, and interestingly also exhibited microbial biodegradability, indicating the possible recyclability of PA54 as a bio-based nylon.[1347]

Partially or fully aromatic polyamides, termed aramids if >85% of the amide linkages are between two aromatic rings, are very high-performance polyamides, with aerospace and military applications such as Kevlar for bulletproof vests. Semi-aromatic polyamides such as PA6T and PA6I, derived from 1,6-HDA with terephthalic or isophthalic acid, respectively, are heat resistant polymers with high melting and glass-transition temperatures, high rigidity, and low water absorption.[1350] Recent work by Shen *et al.* synthesized PA5F and PA10F, novel semi-aromatic polyamides of 2,5-FDCA with 1,5-PeDA and 1,10-decanediamine, respectively.[1351] Both polyamides showed high thermal stability (i.e., up to 380 °C), with PA5F showing a relatively high $T_g$ of 86 °C and PA10F exhibiting a lower $T_g$ of 35 °C, and were identified by the authors as potentially useful materials for bio-based 3D-printing applications.

As the discussed polyamides only utilize the most obvious monomer choices and are fairly recent, this is an active research area, and a range of further bio-based polyamides will emerge in the coming years. Currently, the most interesting novel polyamides subject to further investigation appear to be PA56, PA52, PA54 and PA5F, although the development of additional easily accessible diamines is expected to open up a range of new polyamides to be studied (Figure 102).

### 5.2.3. Polyurethanes.

Polyurethanes (PUs) are a versatile class of polymers with excellent strength-to-weight ratios and energy-absorbing properties.[1253] PUs find applications as elastomers, hard/flexible plastics and soft/rigid foams, within a number of fields including the automotive, industrial and

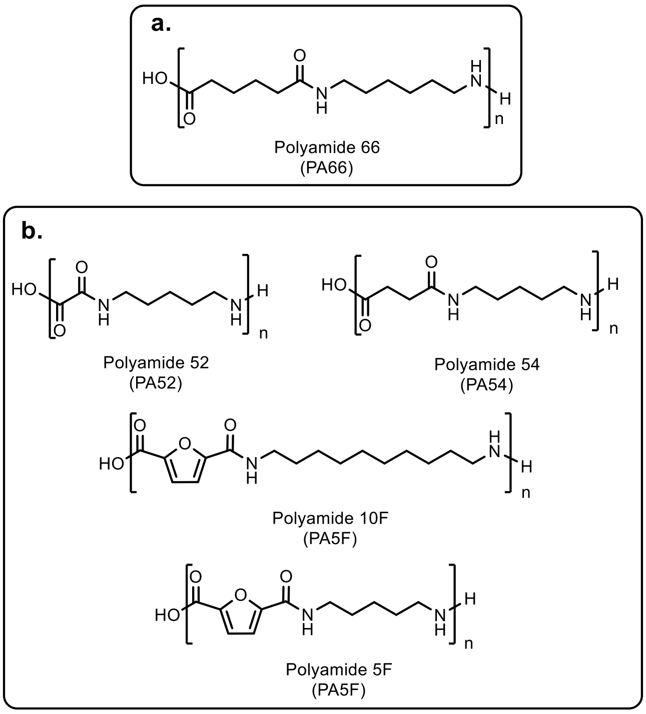


**Figure 102.** (a) One of the most common polyamides, PA66, and (b) some promising bio-based polyamide analogues for the displacement of PA66.

medical fields, with a global market of 24 MT in 2020.[1352−1354] The typical synthesis of PUs involves the catalyzed polyaddition reaction of a diisocyanate with a polyol. As this review mainly focusses on thermoplastic materials, the polyol discussion herein will be limited to diols. The diols chosen for PU synthesis are typically hydroxy-terminated low molecular weight polymers, such as polyethers, polyesters and polycarbonates, which can be readily produced from a range of bio-based sources.[1137] As mentioned in section 5.1.4, conventional PU synthesis suffers from health concerns due to its reactive and toxic nature, in particular when using low molecular weight diisocyanates.[1355,1356] The conventional diisocyanate route is currently the dominant route and would benefit from sustainably sourced diisocyanate monomers.

In anticipation of bio-sourced PU production, the synthesis of so-called non-isocyanate PUs (NIPUs) has rapidly emerged and might present a worthy alternative pathway in the near-future. Indeed, NIPUs have gained tremendous attention in recent years, as was recently reviewed by Khatoon *et al.*[1357] The preparation of cyclic carbonate precursors, discussed in section 5.1.4, and their conversion to carbamates (urethanes) in the presence of diamines can be used to give polyurethanes *via* a step-growth polyaddition reaction (Figure 103a).[1358] The polyaddition of diamines with bifunctional 5-membered cyclic carbonates was first reported in 1957 and produces PU with pendant hydroxy groups.[1253,1359] Notably, the asymmetric nature of the 5-membered cyclic carbonates results in a mixture of two slightly different polymer structures, with either an extra carbon in the backbone or in the alkyl chain of the pendant hydroxy groups. Cyclic carbonates have low toxicity, show biodegradability and are reactive toward amines, which make them very attractive materials to use for NIPU synthesis.[1360] Furthermore, the absence of residual unstable chemicals commonly seen in PU enhance NIPUs with better thermal stability than conventional PU, although residuals hydroxyl groups are known to induce transcarbamoylation reactions.[1361,1362] To avoid pendant hydroxyl groups, ethylene carbonate can be reacted with a diamine and a diol to produce linear polyurethanes and ethylene glycol (Figure 103b).[1363]

Alternatively to the above-mentioned step-growth polymerizations, the ring-opening polymerization (ROP) of aliphatic cyclic urethanes/diurethanes can occur *via* a chain-growth mechanism.[1364] The 5- and 6-membered cyclic urethanes can be produced sustainable in a number of way, including with pressurized $CO_2$ without a catalyst.[1365] However, other cyclic urethanes are either unstable and difficult to form, or too stable for the polymerization reaction to proceed swiftly.[1253]

An additional non-isocyanate route to PU involves the replacement of phosgene with $CO_2$, where aziridines (nitrogen epoxide analogues) react with supercritical $CO_2$, yielding random PU copolymers with a mixture of amine and urethane

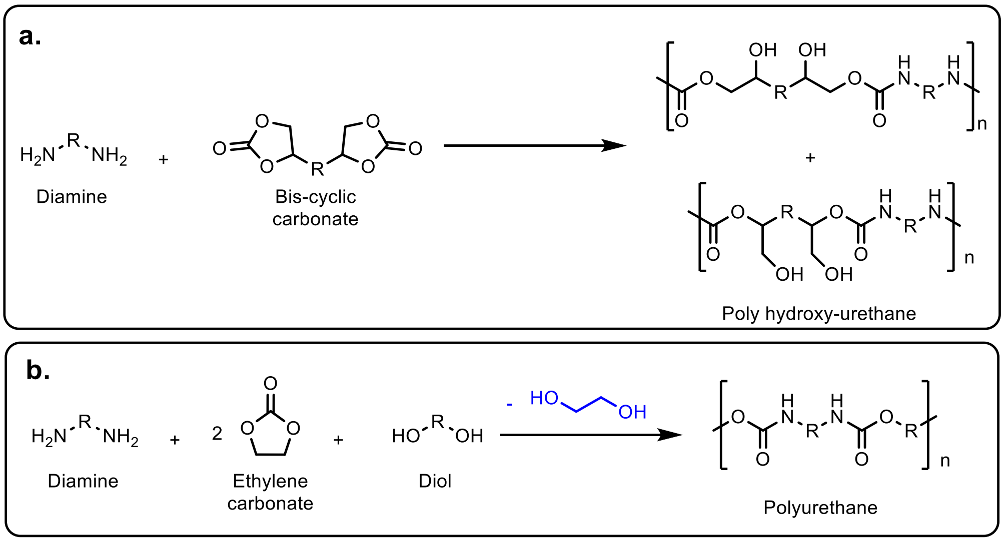


**Figure 103.** Synthesis of non-isocyanate polyurethanes (NIPUs) from (a) the polyaddition of a diamine and a bis-cyclic carbonate, and (b) the polycondensation of a diamine, a diol and ethylene carbonate.

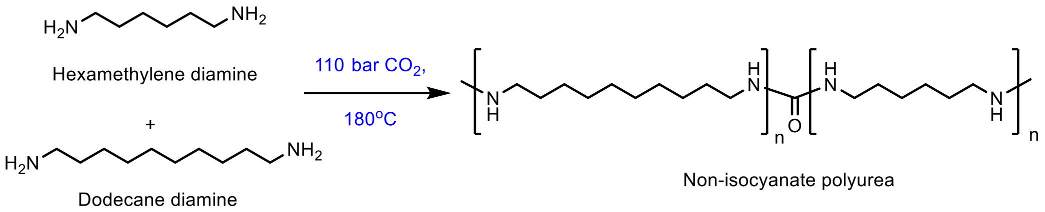


**Figure 104.** Catalyst-free synthesis of non-isocyanate polyureas (NIPUAs) from the reaction of diamines in supercritical $CO_2$.

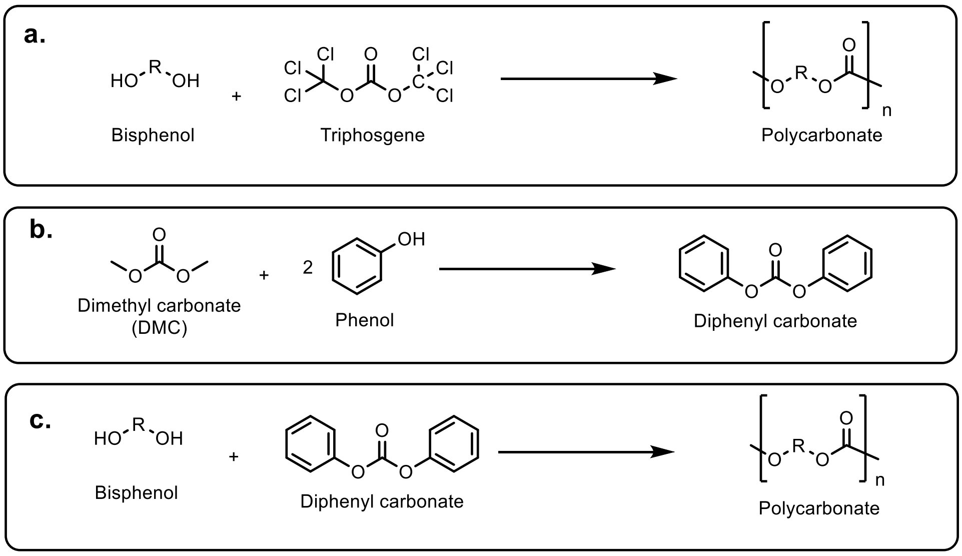


**Figure 105.** (a) Polymerization of bisphenols with toxic triphosgene to give polycarbonates, (b) production of diphenyl carbonate *via* the transesterification of DMC with phenol and (c) use of diphenyl carbonate as a comonomer with bisphenols to give more sustainable polycarbonates.

units.[1253,1366,1367] Ihata *et al.* observed changing LCST behaviour dependent on the $CO_2$ pressure, which was attributed to the increased $CO_2$ pressure causing an increase in urethane content.[1368]

As the most common tunable component in these systems is the diamine, the range of diamines available largely controls the range of PU structures available. A number of cross-linked NIPU systems based on terpenes and vegetable oils have been reported, while linear NIPUs are less commonly the focus of study.[1369,1370] Cramail and co-workers conducted the polyaddition of various diamines with linear bis-carbonates derived from methyl oleate in supercritical $CO_2$ to produce a range of linear NIPUs.[1371] With a Ti-based catalyst, Deepa *et al.* conducted the melt polycondensation of sustainably prepared dicarbamates with diols to produce linear NIPUs, and Meier and co-workers synthesized terpene-based NIPUs in a similar manner.[1278,1372] Khatoon *et al.* recently reviewed the state-of-the-art on NIPUs, albeit with a larger focus on the various applications that NIPUs find use in.[1357]

PUs from an incredibly useful and ubiquitous class of polymers due to their versatility and tunability. With advanced research, the uses of NIPUs are expected to become more widespread and perhaps capable of phasing out toxic diisocyanates and other phosgene derivatives in PU synthesis.

### 5.2.4. Polyureas.

Polyureas (PUas) are an important type of polymer material with structures similar to PUs. PUas are conventionally produced in a manner similar to PUs, through the polyaddition reaction of a diisocyanate with a polyamine, which is typically a diamine in the case of thermoplastic PUas. As such, conventional PUas are faced with similar concerns as conventional PUs with regard to the use of isocyanates. Additionally, there is typically a very narrow processing window between the melting and degradation of isocyanate-based PUas, such that melt processing and recycling the materials is largely ineffective.[1373,1374] The synthesis of non-isocyanate polyureas (NIPUas) has been extensively researched, and a number of routes to thermoplastic NIPUas have been established (Figure 104). These routes typically utilize $CO_2$ either as a comonomer directly or *via* some $CO_2$-derived intermediate, which includes bis-carbamates and carbonates, and they often largely parallel the synthesis routes of NIPUs by using a diamine in place of a diol.[1375−1381]

The direct utilization of $CO_2$ as a comonomer with a diamine has been conducted with a range of catalyst types, including ionic liquids, alkali bases, organic superbases and complex salts, as well as without a catalyst at 180 °C.[1382−1388] However, the obtained molecular weights are typically below 4000 g $mol^{-1}$ due to the water produced in the reaction affecting the equilibrium. Hence, underwhelming physical properties are often obtained due to the high crystallinity caused by strong regular hydrogen bonds.[1389−1391] Recently, Shi *et al.* prepared a series of PUas formed from $CO_2$, HDA and dodecanediamine (DDDA) in a two-step catalyst-free procedure (Figure 104).[1373] While the highest molecular weight observed was still only 4500 g $mol^{-1}$, the particular combination of diamines interrupted the crystalline packing, while maintaining less-regularly ordered hydrogen bonds. Due to this, the material's brittleness was alleviated, and the physical properties exhibited were as good as, if not superior to, previously reported $CO_2$-based PUas, isocyanate-free PUs, PA6 and conventional PUas. Additionally, the copolymers all exhibited a large processing window of ≥85 °C due to their impressive thermal stability and the depression of the two homopolymer melting points observed on the copolymer. To achieve higher molecular weight materials, indirect use of $CO_2$ is required. As mentioned, one such method is the production of dicarbamates from the reaction of bifunctional cyclic carbonates, and the subsequent reaction with a diamine. Alongside making the previously mentioned linear NIPUs, Deepa *et al.* conducted the polyaddition of dicarbamates with diamines to produce linear PUas, and Koning and co-workers employed a non-metal TBD catalyst to prepare similar materials.[1372,1392] An excellent review on the current state of polyurea research was recently published by Santana *et al.*[1393] The work of Shi *et al.* and other similar works have highlighted the exceptional potential for the catalyst-free preparation of bio-based NIPUas directly from a diamine and $CO_2$, requiring only elevated temperatures and pressurized $CO_2$.[1373] Here, the potential for bio-based NIPUas is believed to further expand as additional bio-based diamines are developed and commercialized.

**5.2.5. Polycarbonates.** Polycarbonates (PCs) are a class of polymer with carbonate groups in their backbone. Due to their excellent properties such as ductility, creep resistance, impact resistance and optical transparency, PCs are produced in high volume as engineering plastics for use within sectors such as the construction and automotive industries.[1394,1395] PCs are conventionally produced *via* the reaction of a diol with (tri)phosgene, with the most commonly used diol being bisphenol A (BPA, Figure 105a). Similar to PUs and PUas, the production and use of PCs has several concerns, due to the high toxicity of phosgene and the toxic and environmentally hazardous nature of BPA.[1396,1397] Additionally, both of these components are traditionally derived from petrochemicals.

Biomass sources are seen as a potential route to both avoid the risks associated with BPA and also increase the utilization of sustainable feedstocks for chemical production. The alternative aromatic polyols produced by Garrison *et al.* (Figure 90) were then polymerized to PCs with molecular weights of up to 14 600 g $mol^{-1}$, and $T_g$ values in the range 51−156 °C, hence performing as good as BPA-based PCs (PCBPA) and highlighting the utility of bio-based polycarbonates as replacements for PCBPA. However, the polymerization was conducted with triphosgene, a slightly safer phosgene derivative, in order to closely follow common industrial PC synthesis procedures (Figure 105).[1146]

A number of other bio-based feedstocks have been used to synthesize PCs *via* similar routes utilizing phosgene derivatives, including sugars,[1398] softwood lignin,[1399] eugenol,[1400] ferulic acid[1401] and vanillyl alcohol.[1402]

Despite the sustainability issues of using phosgene-derivatives, bisphenols such as those mentioned present the most straightforward replacements for BPA with lower toxicity bio-based bisphenols in the short term. In the long term, a move toward more sustainable polymerization reactants will likely result in the exploitation of other methods to polycarbonate synthesis, which avoid phosgene derivatives and other petrochemically derived materials. The most common route to bio-based non-phosgene and non-BPA PCs is *via* the reaction of diols with diphenyl carbonate (DPC), which can be sustainably produced through a transesterification of bio-based dimethyl carbonate with bio-based phenol.[1140,1403−1406] For example, novel bio-based diols with rigid cyclic ketals formed from glycerol and diketones were reacted with DPC to give PCs with glass transition and degradation temperatures above 128 and 350 °C, respectively. Similarly, a carvacrol-derived bisphenol was converted into a PC.[1404−1406] Several other routes have been established, including the conversion of a citric acid-based diol to a bis-cyclic carbonate and subsequent step-growth ring-opening polymerization with an additional diol.[1407] Similarly, the chain-growth ring-opening polymerization of fatty acid-based cyclic carbonates,[1408] and the direct polymerization of a limonene oxide with $CO_2$ as a green-phosgene alternative in the presence of a Zn-based catalyst have been reported.[1409] PCs will continue to be developed as the diverse naturally occurring structures seen in bio-based feedstocks are utilized for monomer synthesis, providing great potential for phasing out the use of highly toxic phosgene-derivatives and BPA monomers in the future.

## 6. CONCLUSIONS AND OUTLOOK

Extensive research efforts in developing monomers from sustainable sources are reshaping the field of sustainable plastics. The convenience of obtaining known commodity polymer structures outweighs the additional efforts and costs related to isolation of basic chemicals from biomass and other sustainable resources. The technology for the synthesis of ethanol is already available and enables sustainable production of polyethylene and polypropylene. Similarly, various acrylics and lactones can also be obtained from carbohydrate and fatty acid derivatives. Finally, diacids and diols extracted from sustainable sources enable the synthesis of sustainable polyesters and similar step-growth polymers. The main question now is “are the consumers ready to pay the additional cost?” for the sake of obtaining the same plastics materials from sustainable sources. In 2022, following the sudden global oil and gas supply crisis, fossil fuel prices have more than doubled in less than a year, which may catalyze the methods reported in this review to become more widely available and perhaps more rewarding. Nonetheless, any extra cost associated with the shift toward (more) sustainable monomers is presumed to be compensated by introducing superior material functionality and/or properties.

While this review aims to inspire future developments toward the like-for-like substitution of petrochemicals by sustainable monomers in conventional polymerization processes, it has no intend to discourage fundamental research into creating new types of polymer materials that are derived from renewable resources. This might perhaps offer a more appropriate solution to the pressing needs for sustainable plastics in the long term. However, sustainability is a multifaceted challenge and can only truly be assessed by taking into account the entire life cycle of a plastic material, ranging from how and where monomers are sourced to its impact on the manufacturing process, material use and waste management. Hence, some renewable monomers that are generally considered to be more sustainable might still be outperformed in a life cycle analysis by their conventional petrochemical counterpart when considering one’s specific industrial process and supply chain.

## AUTHOR INFORMATION

### Corresponding Author

**C. Remzi Becer** – *Department of Chemistry, University of Warwick, CV4 7AL Coventry, United Kingdom;* orcid.org/0000-0003-0968-6662; Email: Remzi.Becer@warwick.ac.uk

### Authors

**Graham Hayes** – *Department of Chemistry, University of Warwick, CV4 7AL Coventry, United Kingdom*

**Matthew Laurel** – *Department of Chemistry, University of Warwick, CV4 7AL Coventry, United Kingdom*

**Dan MacKinnon** – *Department of Chemistry, University of Warwick, CV4 7AL Coventry, United Kingdom*

**Tieshuai Zhao** – *Department of Chemistry, University of Warwick, CV4 7AL Coventry, United Kingdom*

**Hannes A. Houck** – *Department of Chemistry, University of Warwick, CV4 7AL Coventry, United Kingdom; Institute of Advanced Study, University of Warwick, CV4 7AL Coventry, United Kingdom;* orcid.org/0000-0001-7602-3784

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.chemrev.2c00354

### Author Contributions

All authors contributed equally in writing the paper.

### Notes

The authors declare no competing financial interest.

### Biographies

Graham Hayes completed his MChem at the University of Southampton in 2013. After that, he worked as an industrial chemist for 6 years before starting a PhD at the University of Warwick under the supervision of Prof. Remzi Becer. His PhD research has focused on the synthesis and analysis of complex poly(2-oxazoline)s structures such as star polymers, cyclic polymers and multiblock polymers.

Matthew Laurel started a PhD in 2020, researching sustainable thiomethacrylate-based polymers in the Becer group at the University of Warwick. Previously, he completed his MChem at the University of Warwick in 2019, with a 3-month international placement at Chalmers University under the supervision of Gunnar Westman, focusing on sustainable polymers from nanocellulose.

Daniel MacKinnon is a PhD student researching sustainable polymers in the Becer group at the University of Warwick. He received his MChem degree in Chemistry from the University of York in 2020, including a year working at Innospec Ltd. He is interested in the research and production of sustainable polymer materials from biomass sources and the synthesis of interesting macromolecular architectures through click chemistry.

Tieshuai Zhao is currently working as a R&D engineer at Huawei Technologies Co.Ltd. He worked on functional polymers and click reactions during his PhD in the Becer group at the University of Warwick. He received his Doctoral degree in Chemistry from the University of Warwick in 2021. He is interested in the synthesis of novel polymeric structures *via* click chemistry and the preparation of functional polymers, also high-performance adhesives.

Dr. Hannes A. Houck obtained a dual PhD degree from Ghent University, Belgium (PhD) and the Karlsruhe Institute of Technology, Germany (Dr. rer. nat.) in 2018. His PhD thesis, supervised by Prof. Filip Du Prez and Prof. Christopher Barner-Kowollik, investigated the on-demand on/off-switching of 1,2,4-triazoline-3,5-dione reactivity with applications in (de)bondable polymer systems. Following postdoctoral research at Ghent University working on light-stabilized dynamic materials, he started as an independent EUTOPIA Science and Innovation Fellow at the University of Warwick, UK in September 2021. Currently, he is looking into the development of new photo-chemistry approaches to form, break and reform cross-linked polymer materials.

Prof. Dr. Remzi Becer has completed his PhD at Eindhoven University of Technology, the Netherlands (2009). He received a Marie Curie Research Fellowship (2009–2011) and joined University of Warwick, UK. He was awarded a Science City Senior Research Fellowship (2011–2013) to start up his independent research group at the same university. He was appointed (2013–2018) as a senior lecturer at Queen Mary, University of London and moved his research group back to the University of Warwick in 2019. He is currently a professor in Sustainable Polymer Chemistry at the University of Warwick and acting as an editor of European Polymer Journal (2018–). For more information visit www.becergroup.com and follow us on Twitter @remzibecer.

## ACKNOWLEDGMENTS

University of Warwick for funding the PhD studies of D.M. and G.H. is acknowledged. H.A.H. acknowledges funding received from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 945380 in the framework of his EUTOPIA-SIF fellowship.

## REFERENCES

(1) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, Use, and Fate of All Plastics Ever Made. *Sci. Adv.* **2017**, 3, No. e1700782.

(2) Chamas, A.; Moon, H.; Zheng, J.; Qiu, Y.; Tabassum, T.; Jang, J. H.; Abu-Omar, M.; Scott, S. L.; Suh, S. Degradation Rates of Plastics in the Environment. *ACS Sus. Chem. Eng.* **2020**, *8*, 3494–3511.

(3) Min, K.; Cuiffi, J. D.; Mathers, R. T. Ranking Environmental Degradation Trends of Plastic Marine Debris Based on Physical Properties and Molecular Structure. *Nat. Commun.* **2020**, *11*, 727.

(4) Mitrano, D. M.; Wagner, M. A Sustainable Future for Plastics Considering Material Safety and Preserved Value. *Nat. Rev. Mater.* **2022**, *7*, 71–73.

(5) Nakajima, H.; Dijkstra, P.; Loos, K. The Recent Developments in Biobased Polymers toward General and Engineering Applications: Polymers That Are Upgraded from Biodegradable Polymers, Analogous to Petroleum-Derived Polymers, and Newly Developed. *Polymers* **2017**, *9*, 523.

(6) Molina-Gutiérrez, S.; Ladmiral, V.; Bongiovanni, R.; Caillol, S.; Lacroix-Desmazes, P. Radical Polymerization of Biobased Monomers in Aqueous Dispersed Media. *Green Chem.* **2019**, *21*, 36–53.

(7) Cywar, R. M.; Rorrer, N. A.; Hoyt, C. B.; Beckham, G. T.; Chen, E. Y. X. Bio-Based Polymers with Performance-Advantaged Properties. *Nat. Rev. Mater.* **2022**, *7*, 83–103.

(8) Tyagi, P.; Agate, S.; Velev, O. D.; Lucia, L.; Pal, L. A Critical Review of the Performance and Soil Biodegradability Profiles of Biobased Natural and Chemically Synthesized Polymers in Industrial Applications. *Environ. Sci. Technol.* **2022**, *56*, 2071–2095.

(9) Ferreira-Filipe, D. A.; Paço, A.; Duarte, A. C.; Rocha-Santos, T.; Patrício Silva, A. L. Are Biobased Plastics Green Alternatives?-a Critical Review. *Int. J. Env. Res. Public Health* **2021**, *18*, 7729.

(10) Cabernard, L.; Pfister, S.; Oberschelp, C.; Hellweg, S. Growing Environmental Footprint of Plastics Driven by Coal Combustion. *Nat. Sus.* **2022**, *5*, 139–148.

(11) Nielsen, T. D.; Hasselbalch, J.; Holmberg, K.; Stripple, J. Politics and the Plastic Crisis: A Review Throughout the Plastic Life Cycle. *WIREs Energy Environ.* **2020**, *9*, No. e360.

(12) Zhu, Y.; Romain, C.; Williams, C. K. Sustainable Polymers from Renewable Resources. *Nature* **2016**, *540*, 354−362.

(13) Isikgor, F. H.; Becer, C. R. Lignocellulosic Biomass: A Sustainable Platform for the Production of Bio-Based Chemicals and Polymers. *Polym. Chem.* **2015**, *6*, 4497−4559.

(14) Haque, F. M.; Ishibashi, J. S. A.; Lidston, C. A. L.; Shao, H.; Bates, F. S.; Chang, A. B.; Coates, G. W.; Cramer, C. J.; Dauenhauer, P. J.; Dichtel, W. R.; et al. Defining the Macromolecules of Tomorrow through Synergistic Sustainable Polymer Research. *Chem. Rev.* **2022**, *122*, 6322−6373.

(15) Métafiot, A.; Kanawati, Y.; Gérard, J.-F.; Defoort, B.; Marić, M. Synthesis of B-Myrcene-Based Polymers and Styrene Block and Statistical Copolymers by Sg1 Nitroxide-Mediated Controlled Radical Polymerization. *Macromolecules* **2017**, *50*, 3101−3120.

(16) Bauer, N.; Brunke, J.; Kali, G. Controlled Radical Polymerization of Myrcene in Bulk: Mapping the Effect of Conditions on the System. *ACS Sus. Chem. Eng.* **2017**, *5*, 10084−10092.

(17) Molina-Gutiérrez, S.; Manseri, A.; Ladmiral, V.; Bongiovanni, R.; Caillol, S.; Lacroix-Desmazes, P. Eugenol: A Promising Building Block for Synthesis of Radically Polymerizable Monomers. *Macromol. Chem. Phys.* **2019**, *220*, 1900179.

(18) Decostanzi, M.; Auvergne, R.; Boutevin, B.; Caillol, S. Biobased Phenol and Furan Derivative Coupling for the Synthesis of Functional Monomers. *Green Chem.* **2019**, *21*, 724−747.

(19) Mitrano, D. M.; Wohlleben, W. Microplastic Regulation Should Be More Precise to Incentivize Both Innovation and Environmental Safety. *Nat. Commun.* **2020**, *11*, 5324.

(20) Law, K. L.; Narayan, R. Reducing Environmental Plastic Pollution by Designing Polymer Materials for Managed End-of-Life. *Nat. Rev. Mater.* **2022**, *7*, 104−116.

(21) Siracusa, V.; Blanco, I. Bio-Polyethylene (Bio-Pe), Bio-Polypropylene (Bio-Pp) and Bio-Poly(Ethylene Terephthalate) (Bio-Pet): Recent Developments in Bio-Based Polymers Analogous to Petroleum-Derived Ones for Packaging and Engineering Applications. *Polymers (Basel)* **2020**, *12*, 1641.

(22) Nguyen, H. T. H.; Qi, P.; Rostagno, M.; Feteha, A.; Miller, S. A. The Quest for High Glass Transition Temperature Bioplastics. *J. Mater. Chem. A* **2018**, *6*, 9298−9331.

(23) Zhang, H.; Xiao, R.; Jin, B.; Xiao, G.; Chen, R. Biomass Catalytic Pyrolysis to Produce Olefins and Aromatics with a Physically Mixed Catalyst. *Bioresour. Technol.* **2013**, *140*, 256−62.

(24) Zacharopoulou, V.; Lemonidou, A. Olefins from Biomass Intermediates: A Review. *Catalysts* **2018**, *8*, 2.

(25) Melchor-Martinez, E. M.; Macias-Garbett, R.; Alvarado-Ramirez, L.; Araujo, R. G.; Sosa-Hernandez, J. E.; Ramirez-Gamboa, D.; Parra-Arroyo, L.; Alvarez, A. G.; Monteverde, R. P. B.; Cazares, K. A. S.; et al. Towards a Circular Economy of Plastics: An Evaluation of the Systematic Transition to a New Generation of Bioplastics. *Polymers (Basel)* **2022**, *14*, 1203.

(26) Zanchin, G.; Leone, G. Polyolefin Thermoplastic Elastomers from Polymerization Catalysis: Advantages, Pitfalls and Future Challenges. *Prog. Polym. Sci.* **2021**, *113*, 101342.

(27) Ammala, A.; Bateman, S.; Dean, K.; Petinakis, E.; Sangwan, P.; Wong, S.; Yuan, Q.; Yu, L.; Patrick, C.; Leong, K. H. An Overview of Degradable and Biodegradable Polyolefins. *Prog. Polym. Sci.* **2011**, *36*, 1015−1049.

(28) Hu, C.; Liu, C.; Liu, Q.; Zhang, H.; Wu, S.; Xiao, R. Effects of Steam to Enhance the Production of Light Olefins from Ex-Situ Catalytic Fast Pyrolysis of Biomass. *Fuel Proc. Technol.* **2020**, *210*, 106562.

(29) Turunc, O.; Montero de Espinosa, L.; Meier, M. A. Renewable Polyethylene Mimics Derived from Castor Oil. *Macromol. Rap. Commun.* **2011**, *32*, 1357−61.

(30) Haussler, M.; Eck, M.; Rothauer, D.; Mecking, S. Closed-Loop Recycling of Polyethylene-Like Materials. *Nature* **2021**, *590*, 423−427.

(31) Johnson, L. K.; Killian, C. M.; Brookhart, M. New Pd(I1)- and Ni(I1)-Based Catalysts for Polymerization of Ethylene and a-Olefins. *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415.

(32) Dias, M. O. S.; Junqueira, T. L.; Cavalett, O.; Pavanello, L. G.; Cunha, M. P.; Jesus, C. D. F.; Maciel Filho, R.; Bonomi, A. Biorefineries for the Production of First and Second Generation Ethanol and Electricity from Sugarcane. *Appl. Energy* **2013**, *109*, 72−78.

(33) Dias, M. O. S.; Junqueira, T. L.; Cavalett, O.; Cunha, M. P.; Jesus, C. D. F.; Mantelatto, P. E.; Rossell, C. E. V.; Maciel Filho, R.; Bonomi, A. Cogeneration in Integrated First and Second Generation Ethanol from Sugarcane. *Chem. Eng. Res. Des.* **2013**, *91*, 1411−1417.

(34) de Carvalho, A. L.; Antunes, C. H.; Freire, F. Economic-Energy-Environment Analysis of Prospective Sugarcane Bioethanol Production in Brazil. *Appl. Energy* **2016**, *181*, 514−526.

(35) Dias, M. O. S.; Modesto, M.; Ensinas, A. V.; Nebra, S. A.; Filho, R. M.; Rossell, C. E. V. Improving Bioethanol Production from Sugarcane: Evaluation of Distillation, Thermal Integration and Cogeneration Systems. *Energy* **2011**, *36*, 3691−3703.

(36) Luo, L.; van der Voet, E.; Huppes, G. Life Cycle Assessment and Life Cycle Costing of Bioethanol from Sugarcane in Brazil. *Renew. Sus. Energy Rev.* **2009**, *13*, 1613−1619.

(37) Kumar, D.; Singh, V. Bioethanol Production from Corn. In *Corn*; Elsevier, 2019; pp 615−631.

(38) Mohanty, S. K.; Swain, M. R. Bioethanol Production from Corn and Wheat: Food, Fuel, and Future. *Bioethanol Production from Food Crops* **2019**, 45−59.

(39) Hettinga, W. G.; Junginger, H. M.; Dekker, S. C.; Hoogwijk, M.; McAloon, A. J.; Hicks, K. B. Understanding the Reductions in Us Corn Ethanol Production Costs: An Experience Curve Approach. *Energy Policy* **2009**, *37*, 190−203.

(40) Tropea, A.; Wilson, D.; Torre, L. G. L.; Curto, R. B. L.; Saugman, P.; Troy-Davies, P.; Dugo, G.; Waldron, K. W. Bioethanol Production from Pineapple Wastes. *J. Food Res.* **2014**, *3*, 199−204.

(41) Weber, C. T.; Trierweiler, L. F.; Trierweiler, J. O. Food Waste Biorefinery Advocating Circular Economy: Bioethanol and Distilled Beverage from Sweet Potato. *J. Clean. Prod.* **2020**, *268*, 121788.

(42) Konti, A.; Kekos, D.; Mamma, D. Life Cycle Analysis of the Bioethanol Production from Food Waste—a Review. *Energies* **2020**, *13*, 5206.

(43) Boluda-Aguilar, M.; Garcia-Vidal, L.; Gonzalez-Castaneda, F. d. P.; Lopez-Gomez, A. Mandarin Peel Wastes Pretreatment with Steam Explosion for Bioethanol Production. *Bioresour. Technol.* **2010**, *101*, 3506−3513.

(44) Winarni, I; Bardant, T.; Hendra, D Enhancement the Added Value of Sengon Wood Waste Pulp as Bioenergy Raw Material for Bioethanol Production. *IOP Conf. Ser.: Earth Environ. Sci.* **2020**, *415*, 012012.

(45) Dan, M.; Senila, L.; Roman, M.; Mihet, M.; Lazar, M. D. From Wood Wastes to Hydrogen - Preparation and Catalytic Steam Reforming of Crude Bio-Ethanol Obtained from Fir Wood. *Renew. Energy* **2015**, *74*, 27−36.

(46) Mendieta, C. M.; Vallejos, M. E.; Felissia, F. E.; Chinga-Carrasco, G.; Area, M. C. Review: Bio-Polyethylene from Wood Wastes. *J. Polym. Environ.* **2020**, *28*, 1−16.

(47) Amorim, H. V.; Lopes, M. L.; de Castro Oliveira, J. V.; Buckeridge, M. S.; Goldman, G. H. Scientific Challenges of Bioethanol Production in Brazil. *Appl. Microbiol. Biotechnol.* **2011**, *91*, 1267−75.

(48) Dias, M. O.; da Cunha, M. P.; Maciel Filho, R.; Bonomi, A.; Jesus, C. D.; Rossell, C. E. Simulation of Integrated First and Second Generation Bioethanol Production from Sugarcane: Comparison between Different Biomass Pretreatment Methods. *J. Ind. Microbiol. Biotechnol.* **2011**, *38*, 955−66.

(49) Dias, M. O.; Junqueira, T. L.; Cavalett, O.; Cunha, M. P.; Jesus, C. D.; Rossell, C. E.; Maciel Filho, R.; Bonomi, A. Integrated Versus Stand-Alone Second Generation Ethanol Production from Sugarcane Bagasse and Trash. *Bioresour. Technol.* **2012**, *103*, 152−61.

(50) Aditiya, H. B.; Mahlia, T. M. I.; Chong, W. T.; Nur, H.; Sebayang, A. H. Second Generation Bioethanol Production: A Critical Review. *Renew. Sus. Energy Rev.* **2016**, *66*, 631−653.

(51) Macrelli, S.; Mogensen, J.; Zacchi, G. Techno-Economic Evaluation of 2nd Generation Bioethanol Production from Sugar Cane Bagasse and Leaves Integrated with the Sugar-Based Ethanol Process. *Biotechnol. Biofuels* **2012**, *5*, 22.

(52) Soccol, C. R.; Vandenberghe, L. P.; Medeiros, A. B.; Karp, S. G.; Buckeridge, M.; Ramos, L. P.; Pitarelo, A. P.; Ferreira-Leitao, V.; Gottschalk, L. M.; Ferrara, M. A.; et al. Bioethanol from Lignocelluloses: Status and Perspectives in Brazil. *Bioresour. Technol.* **2010**, *101*, 4820−5.

(53) Jeevan Kumar, S. P.; Sampath Kumar, N. S.; Chintagunta, A. D. Bioethanol Production from Cereal Crops and Lignocelluloses Rich Agro-Residues: Prospects and Challenges. *SN Appl. Sci.* **2020**, *2*, 1673.

(54) Zabed, H.; Sahu, J. N.; Suely, A.; Boyce, A. N.; Faruq, G. Bioethanol Production from Renewable Sources: Current Perspectives and Technological Progress. *Renew. Sus. Energy Rev.* **2017**, *71*, 475−501.

(55) Lareo, C.; Ferrari, M. D.; Guigou, M.; Fajardo, L.; Larnaudie, V.; Ramirez, M. B.; Martinez-Garreiro, J. Evaluation of Sweet Potato for Fuel Bioethanol Production: Hydrolysis and Fermentation. *SpringerPlus* **2013**, *2*, 493.

(56) Hadi, A. A. a. M. R. Production of Bioethanol from Sweet Sorghum: A Review. *Afr. J. Agric. Res.* **2009**, *4*, 772−780.

(57) Shimokawa, T.; Ishida, M.; Yoshida, S.; Nojiri, M. Effects of Growth Stage on Enzymatic Saccharification and Simultaneous Saccharification and Fermentation of Bamboo Shoots for Bioethanol Production. *Bioresour. Technol.* **2009**, *100*, 6651−4.

(58) Gonçalves, F. A.; Ruiz, H. A.; dos Santos, E. S.; Teixeira, J. A.; de Macedo, G. R. Bioethanol Production from Coconuts and Cactus Pretreated by Autohydrolysis. *Ind. Crops Prod.* **2015**, *77*, 1−12.

(59) Sivamani, S.; Baskar, R. Optimization of Bioethanol Production from Cassava Peel Using Statistical Experimental Design. *Environ. Prog. Sus. Energy* **2015**, *34*, 567−574.

(60) Shanavas, S.; Padmaja, G.; Moorthy, S. N.; Sajeev, M. S.; Sheriff, J. T. Process Optimization for Bioethanol Production from Cassava Starch Using Novel Eco-Friendly Enzymes. *Biomass & Bioenergy* **2011**, *35*, 901−909.

(61) Chen, S.; Xu, Z.; Li, X.; Yu, J.; Cai, M.; Jin, M. Integrated Bioethanol Production from Mixtures of Corn and Corn Stover. *Bioresour. Technol.* **2018**, *258*, 18−25.

(62) Azad, A. K.; Yesmin, N.; Sarker, S. K.; Sattar, A.; Karim, R. Optimum Conditions for Bioethanol Production from Potato of Bangladesh. *Adv. Biosci. Biotechnol.* **2014**, *05*, 501−507.

(63) Razmovski, R.; Vučurović, V. Bioethanol Production from Sugar Beet Molasses and Thick Juice Using Saccharomyces Cerevisiae Immobilized on Maize Stem Ground Tissue. *Fuel* **2012**, *92*, 1−8.

(64) Goshadrou, A.; Karimi, K.; Taherzadeh, M. J. Bioethanol Production from Sweet Sorghum Bagasse by Mucor Hiemalis. *Ind. Crops Prod.* **2011**, *34*, 1219−1225.

(65) Guigou, M.; Lareo, C.; Pérez, L. V.; Lluberas, M. E.; Vázquez, D.; Ferrari, M. D. Bioethanol Production from Sweet Sorghum: Evaluation of Post-Harvest Treatments on Sugar Extraction and Fermentation. *Biomass & Bioenergy* **2011**, *35*, 3058−3062.

(66) Yang, X.; Li, M.; Liu, H.; Ren, L.; Xie, G. Technical Feasibility and Comprehensive Sustainability Assessment of Sweet Sorghum for Bioethanol Production in China. *Sustainability* **2018**, *10*, 731.

(67) Sanchez, O. J.; Cardona, C. A. Trends in Biotechnological Production of Fuel Ethanol from Different Feedstocks. *Bioresour. Technol.* **2008**, *99*, 5270−95.

(68) Ajayo, P. C.; Huang, M.; Zhao, L.; Tian, D.; Jiang, Q.; Deng, S.; Zeng, Y.; Shen, F. Paper Mulberry Fruit Juice: A Novel Biomass Resource for Bioethanol Production. *Bioresourc. Bioprocess.* **2022**, *9*, 3.

(69) Danmaliki, G. I.; Muhammad, A.; Shamsuddeen, A. A.; Usman, B. J. Bioethanol Production from Banana Peels. *J. Environ. Sci. Toxicol. Food Technol.* **2016**, *10*, 56−62.

(70) Shenoy, D.; Pai, A.; Vikas, R. K.; Neeraja, H. S.; Deeksha, J. S.; Nayak, C.; Rao, C. V. A Study on Bioethanol Production from Cashew Apple Pulp and Coffee Pulp Waste. *Biomass & Bioenergy* **2011**, *35*, 4107−4111.

(71) Wang, F.; Jiang, Y.; Guo, W.; Niu, K.; Zhang, R.; Hou, S.; Wang, M.; Yi, Y.; Zhu, C.; Jia, C.; et al. An Environmentally Friendly and Productive Process for Bioethanol Production from Potato Waste. *Biotechnol. Biofuels* **2016**, *9*, 50.

(72) Khawla, B. J.; Sameh, M.; Imen, G.; Donyes, F.; Dhouha, G.; Raoudha, E. G.; Oumèma, N.-E. Potato Peel as Feedstock for Bioethanol Production: A Comparison of Acidic and Enzymatic Hydrolysis. *Ind. Crops Prod.* **2014**, *52*, 144−149.

(73) Chohan, N. A.; Aruwajoye, G. S.; Sewsynker-Sukai, Y.; Gueguim Kana, E. B. Valorisation of Potato Peel Wastes for Bioethanol Production Using Simultaneous Saccharification and Fermentation: Process Optimization and Kinetic Assessment. *Renew. Energy* **2020**, *146*, 1031−1040.

(74) González-García, S.; Morales, P. C.; Gullón, B. Estimating the Environmental Impacts of a Brewery Waste-Based Biorefinery: Bio-Ethanol and Xylooligosaccharides Joint Production Case Study. *Ind. Crops Prod.* **2018**, *123*, 331−340.

(75) Zabed, H.; Faruq, G.; Sahu, J. N.; Azirun, M. S.; Hashim, R.; Boyce, A. N. Bioethanol Production from Fermentable Sugar Juice. *Sci. World J.* **2014**, *2014*, 957102.

(76) Choi, I. S.; Kim, J.-H.; Wi, S. G.; Kim, K. H.; Bae, H.-J. Bioethanol Production from Mandarin (Citrus Unshiu) Peel Waste Using Popping Pretreatment. *Appl. Energy* **2013**, *102*, 204−210.

(77) Choi, I. S.; Lee, Y. G.; Khanal, S. K.; Park, B. J.; Bae, H.-J. A Low-Energy, Cost-Effective Approach to Fruit and Citrus Peel Waste Processing for Bioethanol Production. *Appl. Energy* **2015**, *140*, 65−74.

(78) Abu Tayeh, H.; Najami, N.; Dosoretz, C.; Tafesh, A.; Azaizeh, H. Potential of Bioethanol Production from Olive Mill Solid Wastes. *Bioresour. Technol.* **2014**, *152*, 24−30.

(79) Kim, H. M.; Wi, S. G.; Jung, S.; Song, Y.; Bae, H. J. Efficient Approach for Bioethanol Production from Red Seaweed Gelidium Amansii. *Bioresour. Technol.* **2015**, *175*, 128−34.

(80) Hessami, M. J.; Phang, S. M.; Salleh, A.; Rabiei, R. Evaluation of Tropical Seaweeds as Feedstock for Bioethanol Production. *Int. J. Environ. Sci. Technol.* **2018**, *15*, 977−992.

(81) Han, W.; Liu, Y.; Xu, X.; Huang, J.; He, H.; Chen, L.; Qiu, S.; Tang, J.; Hou, P. Bioethanol Production from Waste Hamburger by Enzymatic Hydrolysis and Fermentation. *J. Clean. Prod.* **2020**, *264*, 121658.

(82) Demiray, E.; Karatay, S. E.; Donmez, G. Improvement of Bioethanol Production from Pomegranate Peels Via Acidic Pretreatment and Enzymatic Hydrolysis. *Environ. Sci. Poll. Res.* **2019**, *26*, 29366−29378.

(83) Ingale, S.; Joshi, S. J.; Gupte, A. Production of Bioethanol Using Agricultural Waste: Banana Pseudo Stem. *Brazil. J. Microbiol.* **2014**, *45*, 885−892.

(84) Dantas, G. A.; Legey, L. F. L.; Mazzone, A. Energy from Sugarcane Bagasse in Brazil: An Assessment of the Productivity and Cost of Different Technological Routes. *Renew. Sus. Energy Rev.* **2013**, *21*, 356−364.

(85) Cardona, C. A.; Quintero, J. A.; Paz, I. C. Production of Bioethanol from Sugarcane Bagasse: Status and Perspectives. *Bioresour. Technol.* **2010**, *101*, 4754−66.

(86) Senila, L.; Kovacs, E.; Scurtu, D. A.; Cadar, O.; Becze, A.; Senila, M.; Levei, E. A.; Dumitras, D. E.; Tenu, I.; Roman, C. Bioethanol Production from Vineyard Waste by Autohydrolysis Pretreatment and Chlorite Delignification Via Simultaneous Saccharification and Fermentation. *Molecules* **2020**, *25*, 2606.

(87) Rodríguez, L. A.; Toro, M. E.; Vazquez, F.; Correa-Daneri, M. L.; Gouiric, S. C.; Vallejo, M. D. Bioethanol Production from Grape and Sugar Beet Pomaces By solid-State Fermentation. *Int. J. Hydrog. Energy* **2010**, *35*, 5914−5917.

(88) Kadam, K. L; McMillan, J. D Availability of Corn Stover as a Sustainable Feedstock for Bioethanol Production. *Bioresour. Technol.* **2003**, *88*, 17−25.

(89) Li, X.; Kim, T. H.; Nghiem, N. P. Bioethanol Production from Corn Stover Using Aqueous Ammonia Pretreatment and Two-Phase Simultaneous Saccharification and Fermentation (Tpssf). *Bioresour. Technol.* **2010**, *101*, 5910−6.

(90) Petrou, E. C.; Pappis, C. P. Bioethanol Production from Cotton Stalks or Corn Stover? A Comparative Study of Their Sustainability Performance. *ACS Sus. Chem. Eng.* **2014**, *2*, 2036−2041.

(91) Akter, S.; Zabed, H. M.; Sahu, J. N.; Chowdhury, F. I.; Faruq, G.; Boyce, A. N.; Qi, X. Bioethanol Production from Water-Soluble and Structural Carbohydrates of Normal and High Sugary Corn Stovers Harvested at Three Growth Stages. *Energy Convers. Manag.* **2020**, *221*, 113104.

(92) Liu, H.; Pang, B.; Zhao, Y.; Lu, J.; Han, Y.; Wang, H. Comparative Study of Two Different Alkali-Mechanical Pretreatments of Corn Stover for Bioethanol Production. *Fuel* **2018**, *221*, 21−27.

(93) del Río, P. G.; Gullón, P.; Rebelo, F. R.; Romaní, A.; Garrote, G.; Gullón, B. A Whole-Slurry Fermentation Approach to High-Solid Loading for Bioethanol Production from Corn Stover. *Agron.* **2020**, *10*, 1790.

(94) Wang, M.; Zhou, D.; Wang, Y.; Wei, S.; Yang, W.; Kuang, M.; Ma, L.; Fang, D.; Xu, S.; Du, S.-k. Bioethanol Production from Cotton Stalk: A Comparative Study of Various Pretreatments. *Fuel* **2016**, *184*, 527−532.

(95) Dimos, K.; Paschos, T.; Louloudi, A.; Kalogiannis, K. G.; Lappas, A. A.; Papayannakos, N.; Kekos, D.; Mamma, D. Effect of Various Pretreatment Methods on Bioethanol Production from Cotton Stalks. *Fermentation* **2019**, *5*, 5−16.

(96) Kumar, P.; Kumar, V.; Kumar, S.; Singh, J.; Kumar, P. Bioethanol Production from Sesame (Sesamum Indicum L.) Plant Residue by Combined Physical, Microbial and Chemical Pretreatments. *Bioresour. Technol.* **2020**, *297*, 122484.

(97) Yoswathana, N.; Phuriphipat, P.; Treyawutthiwat, P.; Eshtiaghi, M. N. Bioethanol Production from Rice Straw. *Energy Res. J.* **2010**, *1*, 26−31.

(98) Belal, E. B. Bioethanol Production from Rice Straw Residues. *Brazil. J. Microbiol.* **2013**, *44*, 225−234.

(99) Binod, P.; Sindhu, R.; Singhania, R. R.; Vikram, S.; Devi, L.; Nagalakshmi, S.; Kurien, N.; Sukumaran, R. K.; Pandey, A. Bioethanol Production from Rice Straw: An Overview. *Bioresour. Technol.* **2010**, *101*, 4767−74.

(100) Georgieva, T. I.; Mikkelsen, M. J.; Ahring, B. K. Ethanol Production from Wet-Exploded Wheat Straw Hydrolysate by Thermophilic Anaerobic Bacterium Thermoanaerobacter Bg1l1 in a Continuous Immobilized Reactor. *Appl. Microbiol. Biotechnol.* **2008**, *145*, 99−110.

(101) Tamburini, E.; Bernardi, T.; Castaldelli, G.; Tumiatti, G.; Ferro, S. Green Electrochemical Approach for Delignification of Wheat Straw in Second-Generation Bioethanol Production. *Energy Environ. Sci.* **2011**, *4*, 551−557.

(102) Mohapatra, S.; Mishra, C.; Behera, S. S.; Thatoi, H. Application of Pretreatment, Fermentation and Molecular Techniques for Enhancing Bioethanol Production from Grass Biomass - a Review. *Renew. Sus. Energy Rev.* **2017**, *78*, 1007−1032.

(103) Martín, M.; Grossmann, I. E. Optimal Simultaneous Production of I-Butene and Ethanol from Switchgrass. *Biomass & Bioenergy* **2014**, *61*, 93−103.

(104) Tan, J. S.; Phapugrangkul, P.; Lee, C. K.; Lai, Z.-W.; Abu Bakar, M. H.; Murugan, P. Banana Frond Juice as Novel Fermentation Substrate for Bioethanol Production by Saccharomyces Cerevisiae. *Biocat. & Agric. Biotechnol.* **2019**, *21*, 101293.

(105) Muñoz, C.; Mendonça, R.; Baeza, J.; Berlin, A.; Saddler, J.; Freer, J. Bioethanol Production from Bio- Organosolv Pulps Ofpinus Radiata Andacacia Dealbata. *J. Chem. Technol. Biotechnol.* **2007**, *82*, 767−774.

(106) Lee, I.; Yu, J.-H. Design of Hydrothermal and Subsequent Lime Pretreatment for Fermentable Sugar and Bioethanol Production from Acacia Wood. *Renew. Energy* **2021**, *174*, 170−177.

(107) Zhang, J.; Liu, J.; Kou, L.; Zhang, X.; Tan, T. Bioethanol Production from Cellulose Obtained from the Catalytic Hydro-Deoxygenation (Lignin-First Refined to Aviation Fuel) of Apple Wood. *Fuel* **2019**, *250*, 245−253.

(108) Cunha, M.; Romani, A.; Carvalho, M.; Domingues, L. Boosting Bioethanol Production from Eucalyptus Wood by Whey Incorporation. *Bioresour. Technol.* **2018**, *250*, 256−264.

(109) Romaní, A.; Garrote, G.; Ballesteros, I.; Ballesteros, M. Second Generation Bioethanol from Steam Exploded Eucalyptus Globulus Wood. *Fuel* **2013**, *111*, 66−74.

(110) Barbanera, M.; Lascaro, E.; Foschini, D.; Cotana, F.; Buratti, C. Optimization of Bioethanol Production from Steam Exploded Hornbeam Wood (Ostrya Carpinifolia) by Enzymatic Hydrolysis. *Renew. Energy* **2018**, *124*, 136−143.

(111) Baba, Y.; Tanabe, T.; Shirai, N.; Watanabe, T.; Honda, Y.; Watanabe, T. Pretreatment of Japanese Cedar Wood by White Rot Fungi and Ethanolysis for Bioethanol Production. *Biomass & Bioenergy* **2011**, *35*, 320−324.

(112) Khoshnevisan, B.; Shafiei, M.; Rajaeifar, M. A.; Tabatabaei, M. Biogas and Bioethanol Production from Pinewood Pre-Treated with Steam Explosion and N-Methylmorpholine-N-Oxide (Nmmo): A Comparative Life Cycle Assessment Approach. *Energy* **2016**, *114*, 935−950.

(113) Macedo, I. C.; Seabra, J. E. A.; Silva, J. E. A. R. Green House Gases Emissions in the Production and Use of Ethanol from Sugarcane in Brazil: The 2005/2006 Averages and a Prediction for 2020. *Biomass & Bioenergy* **2008**, *32*, 582−595.

(114) Morschbacker, A. Bio-Ethanol Based Ethylene. *Polym. Rev.* **2009**, *49*, 79−84.

(115) Šantek, B.; Gwehenberger, G.; Šantek, M. I.; Narodoslawsky, M.; Horvat, P. Evaluation of Energy Demand and the Sustainability of Different Bioethanol Production Processes from Sugar Beet. *Resour., Conserv., Recycl.* **2010**, *54*, 872−877.

(116) Moodley, P.; Gueguim Kana, E. B. Bioethanol Production from Sugarcane Leaf Waste: Effect of Various Optimized Pretreatments and Fermentation Conditions on Process Kinetics. *Biotechnol. Rep. (Amst)* **2019**, *22*, No. e00329.

(117) Duarte, A.; Uribe, J. C.; Sarache, W.; Calderón, A. Economic, Environmental, and Social Assessment of Bioethanol Production Using Multiple Coffee Crop Residues. *Energy* **2021**, *216*, 119170.

(118) Guerrero, A. B.; Ballesteros, I.; Ballesteros, M. The Potential of Agricultural Banana Waste for Bioethanol Production. *Fuel* **2018**, *213*, 176−185.

(119) Choi, I. S.; Kim, Y. G.; Jung, J. K.; Bae, H.-J. Soybean Waste (Okara) as a Valorization Biomass for the Bioethanol Production. *Energy* **2015**, *93*, 1742−1747.

(120) Raja Sathendra, E.; Baskar, G.; Praveenkumar, R.; Gnansounou, E. Bioethanol Production from Palm Wood Using Trichoderma Reesei and Kluveromyces Marxianus. *Bioresour. Technol.* **2019**, *271*, 345−352.

(121) Lee, S. J.; Kim, H. J.; Cho, E. J.; Song, Y.; Bae, H. J. Isolation and Characterization of Lignin from the Oak Wood Bioethanol Production Residue for Adhesives. *Int. J. Biol. Macromol.* **2015**, *72*, 1056−62.

(122) Domínguez-Bocanegra, A. R.; Torres-Muñoz, J. A.; López, R. A. Production of Bioethanol from Agro-Industrial Wastes. *Fuel* **2015**, *149*, 85−89.

(123) Shamsul, N. S.; Kamarudin, S. K.; Rahman, N. A.; Kofli, N. T. An Overview on the Production of Bio-Methanol as Potential Renewable Energy. *Renew. Sus. Energy Rev.* **2014**, *33*, 578−588.

(124) Khattak, W. A.; Khan, T.; Ha, J. H.; Ul-Islam, M.; Kang, M. K.; Park, J. K. Enhanced Production of Bioethanol from Waste of Beer Fermentation Broth at High Temperature through Consecutive Batch Strategy by Simultaneous Saccharification and Fermentation. *Eznyme Microb. Technol.* **2013**, *53*, 322−30.

(125) Le Van Mao, R.; Levesque, P.; McLaughlin, G.; Dao, L. H. Ethylene from Ethanol over Zeolite Catalysts. *Appl. Catal.* **1987**, *34*, 163−179.

(126) Zaki, T. Catalytic Dehydration of Ethanol Using Transition Metal Oxide Catalysts. *J. Colloid Interface Sci.* **2005**, *284*, 606−13.

(127) Varisli, D.; Dogu, T.; Dogu, G. Ethylene and Diethyl-Ether Production by Dehydration Reaction of Ethanol over Different Heteropolyacid Catalysts. *Chem. Eng. Sci.* **2007**, *62*, 5349−5352.

(128) Pearson, D. E.; Tanner, R. D.; Picciotto, I. D.; Sawyer, J. S.; Cleveland, J. H. Phosphoric Acid Systems. 2. Catalytic Conversion of Fermentation Ethanol to Ethylene. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 734−740.

(129) Haber, J.; Pamin, K.; Matachowski, L.; Napruszewska, B.; Połtowicz, J. Potassium and Silver Salts of Tungstophosphoric Acid as Catalysts in Dehydration of Ethanol and Hydration of Ethylene. *J. Catal.* **2002**, *207*, 296−306.

(130) Le Van Mao, R.; Nguyen, T. M.; McLaughlin, G. P The Bioethanol-to-Ethylene (B.E.T.E.) Process. *Appl. Catal.* **1989**, *48*, 265−277.

(131) Vazquez, P.; Pizzio, L.; Caceres, C.; Blanco, M.; Thomas, H.; Alesso, E.; Finkielsztein, L.; Lantano, B.; Moltrasio, G.; Aguirre, J. Silica-Supported Heteropolyacids as Catalysts in Alcohol Dehydration Reactions. *J. Mol. Catal. A: Chem.* **2000**, *161*, 223−232.

(132) Hu, Y.; Zhan, N.; Dou, C.; Huang, H.; Han, Y.; Yu, D.; Hu, Y. Selective Dehydration of Bio-Ethanol to Ethylene Catalyzed by Lanthanum-Phosphorous-Modified Hzsm-5: Influence of the Fusel. *Biotechnol. J.* **2010**, *5*, 1186−91.

(133) Keil, F. J.; Rieckmann, C. Optimization of Three-Dimensional Catalyst Pore Structures. *Chem. Eng. Sci.* **1994**, *49*, 4811−4822.

(134) Yakovleva, I. S.; Banzaraktsaeva, S. P.; Ovchinnikova, E. V.; Chumachenko, V. A.; Isupova, L. A. Catalytic Dehydration of Bioethanol to Ethylene. *Catal. Ind.* **2016**, *8*, 152−167.

(135) Ivanova, S.; Vanhaecke, E.; Dreibine, L.; Louis, B.; Pham, C.; Pham-Huu, C. Binderless Hzsm-5 Coating on Β-Sic for Different Alcohols Dehydration. *Appl. Catal. A: General* **2009**, *359*, 151−157.

(136) Bi, J.; Guo, X.; Liu, M.; Wang, X. High Effective Dehydration of Bio-Ethanol into Ethylene over Nanoscale Hzsm-5 Zeolite Catalysts. *Catal. Today* **2010**, *149*, 143−147.

(137) Zhang, X.; Wang, R.; Yang, X.; Zhang, F. Comparison of Four Catalysts in the Catalytic Dehydration of Ethanol to Ethylene. *Micropor. Mesopor. Mater.* **2008**, *116*, 210−215.

(138) Lok, B. M.; Messina, C. A.; Patton, R. L.; Gajek, R. T.; Cannan, T. R.; Flanigen, E. M. Silicoaluminophosphate Molecular Sieves: Another New Class of Microporous Crystalline Inorganic Solids. *J. American Chem. Soc.* **1984**, *106*, 6092−6093.

(139) Ramesh, K.; Hui, L. M.; Han, Y.-F.; Borgna, A. Structure and Reactivity of Phosphorous Modified H-Zsm-5 Catalysts for Ethanol Dehydration. *Catal. Commun.* **2009**, *10*, 567−571.

(140) Vinek, H.; Lercher, J.A.; Noller, H. Acid-Base Proerties of Silica-Alumina Oxides Derived from Nax Zeolites - Part Iii: Catalytic Activity in Dehydration of Alcohols and in Isomerization of but-1-Ene. *J. Mol. Catal.* **1985**, *30*, 353−359.

(141) Mostafa, M.R.; Youssef, A.M.; Hassan, S.M. Conversion of Ethanol and Isopropanol on Alumina, Titania and Alumina-Titania Catalysts. *Mater. Lett.* **1991**, *12*, 207−213.

(142) Danilevich, V. V.; Isupova, L. A.; Paukshtis, E. A.; Ushakov, V. A. Effect of Modifying Alumina Desiccants with Sulfuric Acid on Their Physicochemical Properties. *Kinet. Catal.* **2014**, *55*, 372−379.

(143) Di Cosimo, J.I.; Dıez, V.K.; Xu, M.; Iglesia, E.; Apesteguıa, C.R. Apesteguia, Structure and Surface and Catalytic Properties of Mg-Al Basic Oxides. *J. Catal.* **1998**, *178*, 499−510.

(144) Doheim, M.M; Hanafy, S.A; El-Shobaky, G.A Catalytic Conversion of Ethanol and Isopropanol over the Mn2o3/Al2o3 System Doped with Na2o. *Mater. Lett.* **2002**, *55*, 304−311.

(145) Tursunov, O.; Kustov, L.; Tilyabaev, Z. Catalytic Activity of H-Zsm-5 and Cu-Hzsm-5 Zeolites of Medium Sio2/Al2o3 Ratio in Conversion of N-Hexane to Aromatics. *J. Petrol. Sci. Eng.* **2019**, *180*, 773−778.

(146) Phillips, C. B.; Datta, R. Production of Ethylene from Hydrous Ethanol on H-Zsm-5 under Mild Conditions. *Ind. Eng. Chem. Res.* **1997**, *36*, 4466−4475.

(147) de Reviere, A.; Vandevyvere, T.; Sabbe, M. K.; Verberckmoes, A. Renewable Butene Production through Dehydration Reactions over Nano-Hzsm-5/Γ-Al2o3 Hybrid Catalysts. *Catalysts* **2020**, *10*, 879.

(148) El-Shobaky, G.A; Doheim, M.M; Ghozza, A.M; El-Boohy, H.A El-Boohy Catalytic Conversion of Ethanol over Co3o4/Mgo System Treated with G-Irradiation. *Mater. Lett.* **2002**, *57*, 525−531.

(149) Abu-Zied, B.M; El-Awad, A.M The Synergism Ofcadmium on the Catalytic Activity of Cd-Cr-O System Ii. Ethanol Decomposition, Catalysts Reducibility, and in Situ Electrical Conductivity Measurements. *J. Mol. Catal. A: Chem.* **2001**, *176*, 227−246.

(150) Doheim, M.M.; El-Shobaky, H.G. Catalytic Conversion of Ethanol and Iso-Propanol over Zno-Treated Co3o4/Al2o3 Solids. *Colloids Surf., A Physicochem. Eng. Asp.* **2002**, *204*, 169−174.

(151) El-Katatny, E. A.; Halawy, S. A.; Mohamed, M. A.; Zaki, M. I. Recovery of Ethene-Selective Feox/Al2o3 Ethanol Dehydration Catalyst from Industrial Chemical Wastes. *Appl. Catal. A: General* **2000**, *199*, 83−92.

(152) Bagshaw, S. A.; Pinnavaia, T. J. Mesoporous Alumina Molecular Sieves. *Angew. Chem., Int. Ed.* **1996**, *35*, 1102−1105.

(153) El-Sharkawy, E.A.; El-Hakam, S.A.; Samra, S.E. Effect of Thermal Treatment on the Various Properties of Iron(Iii)-Aluminum (Iii) Coprecipitated Hydroxide System. *Mater. Lett.* **2000**, *42*, 331−338.

(154) Tarrés, Q.; Melbø, J. K.; Delgado-Aguilar, M.; Espinach, F. X.; Mutjé, P.; Chinga-Carrasco, G. Bio-Polyethylene Reinforced with Thermomechanical Pulp Fibers: Mechanical and Micromechanical Characterization and Its Application in 3d-Printing by Fused Deposition Modelling. *Compos. B. Eng.* **2018**, *153*, 70−77.

(155) Tarres, Q.; Ardanuy, M. Evolution of Interfacial Shear Strength and Mean Intrinsic Single Strength in Biobased Composites from Bio-Polyethylene and Thermo-Mechanical Pulp-Corn Stover Fibers. *Polymers (Basel)* **2020**, *12*, 1308.

(156) Hanken, R. B. L.; Arimatéia, R. R.; Farias, G. M. G.; Agrawal, P.; Santana, L. N. L.; Freitas, D. M. G.; de Mélo, T. J. A. Effect of Natural and Expanded Vermiculite Clays on the Properties of Eco-Friendly Biopolyethylene-Vermiculite Clay Biocomposites. *Compos. B. Eng.* **2019**, *175*, 107184.

(157) Neuhoff, U.; Sick, S.; Lohr, I.; Sander, D.; Jansen, B.; Hally, S. Artificial Turf Fiber from Renewable Polyethylene. EP 3315640A1, 2016.

(158) Natarajan, R.; Chee, Y.; Smith, L. Method and Formulation for Renewable Polyethylene Foams. US 20200062915, 2018.

(159) Devisme, S.; Pradel, J.-L.; Le, G.; Roussel, T. Production of Grafted Polyethylene from Renewable Materials the Obtained Polyethylene and Uses Thereof. CN 102164972A, 2008.

(160) Roy, P. K.; Hakkarainen, M.; Varma, I. K.; Albertsson, A. C. Degradable Polyethylene: Fantasy or Reality. *Environ. Sci. Technol.* **2011**, *45*, 4217−27.

(161) Chang, C.-C.; Emrick, T. Functional Polyolefins Containing Disulfide and Phosphoester Groups: Synthesis and Orthogonal Degradation. *Macromolecules* **2014**, *47*, 1344−1350.

(162) Phung, T. K.; Pham, T. L. M.; Vu, K. B.; Busca, G. (Bio)Propylene Production Processes: A Critical Review. *J. Environ. Chem. Eng.* **2021**, *9*, 105673.

(163) Koempel, H.; Liebner, W. Lurgi's Methanol to Propylene (Mtp®) Report on a Successful Commercialisation. In *Natural Gas Conversion VIII*; Noronha, F. B., Schmal, M., Sousa-Aguiar, E. F., Eds.; Elsevier B.V., 2007.

(164) Yu, L.; Yuan, J.; Zhang, Q.; Liu, Y. M.; He, H. Y.; Fan, K. N.; Cao, Y. Propylene from Renewable Resources: Catalytic Conversion of Glycerol into Propylene. *ChemSusChem* **2014**, *7*, 743−7.

(165) Chen, J. Q.; Bozzano, A.; Glover, B.; Fuglerud, T.; Kvisle, S. Recent Advancements in Ethylene and Propylene Production Using the Uop/Hydro Mto Process. *Catal. Today* **2005**, *106*, 103−107.

(166) Minteer, S. D. Biochemical Production of Other Bioalcohols: Biomethanol, Biopropanol, Bioglycerol, and Bioethylene Glycol. *Handbook of Biofuels Production* **2011**, 258−265.

(167) Wang, D.; Xiao, R.; Zhang, H.; He, G. Comparison of Catalytic Pyrolysis of Biomass with Mcm-41 and Cao Catalysts by Using Tga-Ftir Analysis. *J. Anal. Appl. Pyrolysis.* **2010**, *89*, 171−177.

(168) West, R. M.; Braden, D. J.; Dumesic, J. A. Dehydration of Butanol to Butene over Solid Acid Catalysts in High Water Environments. *J. Catal.* **2009**, *262*, 134−143.

(169) Hanaoka, T.; Fujimoto, S.; Kihara, H. Evaluation of N-Butene Synthesis from Dimethyl Ether in the Production of 1,3-Butadiene from Lignin: A Techno-Economic Analysis. *Renew. Energy* **2021**, *163*, 964−973.

(170) Zhang, J.; Wegener, E. C.; Samad, N. R.; Harris, J. W.; Unocic, K. A.; Allard, L. F.; Purdy, S.; Adhikari, S.; Cordon, M. J.; Miller, J. T.; et al. Isolated Metal Sites in Cu-Zn-Y/Beta for Direct and Selective Butene-Rich C3+ Olefin Formation from Ethanol. *ACS Catal.* **2021**, *11*, 9885−9897.

(171) Cordon, M. J.; Zhang, J.; Purdy, S. C.; Wegener, E. C.; Unocic, K. A.; Allard, L. F.; Zhou, M.; Assary, R. S.; Miller, J. T.; Krause, T. R.; et al. Selective Butene Formation in Direct Ethanol-to-C3+-Olefin Valorization over Zn-Y/Beta and Single-Atom Alloy Composite Catalysts Using in Situ-Generated Hydrogen. *ACS Catal.* **2021**, *11*, 7193−7209.

(172) Dagle, V. L.; Winkelman, A. D.; Jaegers, N. R.; Saavedra-Lopez, J.; Hu, J.; Engelhard, M. H.; Habas, S. E.; Akhade, S. A.; Kovarik, L.; Glezakou, V.-A.; et al. Single-Step Conversion of Ethanol to N-Butene over Ag-Zro2/Sio2 Catalysts. *ACS Catal.* **2020**, *10*, 10602−10613.

(173) Avasthi, K.; Bohre, A.; Grilc, M.; Likozar, B.; Saha, B. Advances in Catalytic Production Processes of Biomass-Derived Vinyl Monomers. *Catal. Sci. Technol.* **2020**, *10*, 5411−5437.

(174) Chaukura, N.; Gwenzi, W.; Bunhu, T.; Ruziwa, D. T.; Pumure, I. Potential Uses and Value-Added Products Derived from Waste Polystyrene in Developing Countries: A Review. *Resour., Conserv., Recycl.* **2016**, *107*, 157−165.

(175) Schutyser, W.; Renders, T.; Van den Bosch, S.; Koelewijn, S. F.; Beckham, G. T.; Sels, B. F. Chemicals from Lignin: An Interplay of Lignocellulose Fractionation, Depolymerisation, and Upgrading. *Chem. Soc. Rev.* **2018**, *47*, 852−908.

(176) Rinaldi, R.; Jastrzebski, R.; Clough, M. T.; Ralph, J.; Kennema, M.; Bruijnincx, P. C.; Weckhuysen, B. M. Paving the Way for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis. *Angew. Chem., Int. Ed.* **2016**, *55*, 8164−215.

(177) Carlson, T. R.; Tompsett, G. A.; Conner, W. C.; Huber, G. W. Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks. *Top. Catal.* **2009**, *52*, 241−252.

(178) Fan, M.; Jiang, P.; Bi, P.; Deng, S.; Yan, L.; Zhai, Q.; Wang, T.; Li, Q. Directional Synthesis of Ethylbenzene through Catalytic Transformation of Lignin. *Bioresour. Technol.* **2013**, *143*, 59−67.

(179) Li, L.; Dong, L.; Liu, X.; Guo, Y.; Wang, Y. Selective Production of Ethylbenzene from Lignin Oil over Feox Modified Ru/Nb2o5 Catalyst. *Appl. Catal. B: Environ.* **2020**, *260*, 118143.

(180) Luo, Z.; Qin, S.; Chen, S.; Hui, Y.; Zhao, C. Selective Conversion of Lignin to Ethylbenzene. *Green Chem.* **2020**, *22*, 1842−1850.

(181) Wang, A.; Song, H. Maximizing the Production of Aromatic Hydrocarbons from Lignin Conversion by Coupling Methane Activation. *Bioresour. Technol.* **2018**, *268*, 505−513.

(182) Degannes, P. N.; Ruthven, D. M. The Oxidative Dehydrogenation of Ethylbenzene to Styrene. *Canad. J. Chem. Eng.* **1979**, *57*, 627−630.

(183) Sugino, M.-o.; Shimada, H.; Turuda, T.; Miura, H.; Ikenaga, N.; Suzuki, T. Oxidative Dehydrogenation of Ethylbenzene with Carbon Dioxide. *Appl. Catal. A: General* **1995**, *121*, 125−137.

(184) Mukherjee, D.; Park, S.-E.; Reddy, B. M. Co2 as a Soft Oxidant for Oxidative Dehydrogenation Reaction: An Eco Benign Process for Industry. *J. CO2 Util.* **2016**, *16*, 301−312.

(185) Yoo, J. S.; Lin, P. S.; Elfline, S. D. Gas-Phase Oxygen Oxidations of Alkylaromatics over Cvd Fe/Mo/Borosilicate Molecular Sieve. Ii. The Role of Carbon Dioxide as a Co-Oxidant. *Appl. Catal. A: General* **1993**, *106*, 259−273.

(186) Burri, A.; Jiang, N.; Yahyaoui, K.; Park, S.-E. Ethylbenzene to Styrene over Alkali Doped Tio 2 -Zro 2 with Co 2 as Soft Oxidant. *Appl. Catal. A: General* **2015**, *495*, 192−199.

(187) Zhang, L.; Wu, Z.; Nelson, N. C.; Sadow, A. D.; Slowing, I. I.; Overbury, S. H. Role of Co2 as a Soft Oxidant for Dehydrogenation of Ethylbenzene to Styrene over a High-Surface-Area Ceria Catalyst. *ACS Catal.* **2015**, *5*, 6426−6435.

(188) Sun, A.; Qin, Z.; Chen, S.; Wang, J. Role of Carbon Dioxide in the Ethylbenzene Dehydrogenation Coupled with Reverse Water-Gas Shift. *J. Mol. Catal. A: Chem.* **2004**, *210*, 189−195.

(189) Gupta, N.; Wang, Q.; Wen, G.; Su, D. Nanodiamonds for Catalytic Reactions. In *Nanodiamonds*; Elsevier Inc., 2017; pp 439−463.

(190) Kafafi, Z. H.; Hauge, R. H.; Billups, W. E.; Margrave, J. L. Carbon Dioxide Activation by Alkali Metals. 2. Infrared Spectra of M +C02 and M22+C021 2∼ in Argon and Nitrogen Matrices. *Inorg. Chem.* **1984**, *23*, 177−183.

(191) Nederlof, C.; Kapteijn, F.; Makkee, M. Catalysed Ethylbenzene Dehydrogenation in Co2 or N2—Carbon Deposits as the Active Phase. *Appl. Catal. A: General* **2012**, *417-418*, 163−173.

(192) Zhu, C.; Chen, S.; Pan, D.; Cui, X.; Qiao, Y.; Li, R. Ordered Mesoporous Alumina-Supported Vanadium Oxides as an Efficient Catalyst for Ethylbenzene Dehydrogenation to Styrene with Co2. *Catal. Commun.* **2018**, *115*, 12−16.

(193) Kainthla, I.; Ramesh Babu, G. V.; Bhanushali, J. T.; Keri, R. S.; Rama Rao, K. S.; Nagaraja, B. M. Vapor-Phase Dehydrogenation of Ethylbenzene to Styrene over a V2o5/Tio2-Al2o3 Catalyst with Co2. *New J. Chem.* **2017**, *41*, 4173−4181.

(194) Betiha, M. A.; Rabie, A. M.; Elfadly, A. M.; Yehia, F. Z. Microwave Assisted Synthesis of a Vo -Modified Disordered Mesoporous Silica for Ethylbenzene Dehydrogenation in Presence of Co2. *Micropor. Mesopor. Mater.* **2016**, *222*, 44−54.

(195) Burri, D. R.; Choi, K. M.; Han, D.-S.; Koo, J.-B.; Park, S.-E. Co2 Utilization as an Oxidant in the Dehydrogenation of Ethylbenzene to Styrene over Mno2-Zro2 Catalysts. *Catal. Today* **2006**, *115*, 242−247.

(196) Burri, D. R.; Choi, K.-M.; Han, S.-C.; Burri, A.; Park, S.-E. Selective Conversion of Ethylbenzene into Styrene over K2o/Tio2-Zro2 Catalysts: Unified Effects of K2o and Co2. *J. Mol. Catal. A: Chem.* **2007**, *269*, 58−63.

(197) Kainthla, I.; Babu, G. V. R.; Bhanushali, J. T.; Rao, K. S. R.; Nagaraja, B. M. Development of Stable Moo 3 /Tio 2 -Al 2 O 3 Catalyst for Oxidative Dehydrogenation of Ethylbenzene to Styrene Using Co 2 as Soft Oxidant. *J. CO2 Util.* **2017**, *18*, 309−317.

(198) Madduluri, V. R.; Nagaiah, P.; Prathap, C.; Vasikerappa, K.; Nagu, A.; David Raju, B.; Rama Rao, K. S. Synergistic Interface between Co3o4 and Mgal2o4 in Co2 Assisted Continuous Vapour Phase Oxidative Dehydrogenation of Ethylbenzene to Styrene Monomer. *Arab. J. Chem.* **2020**, *13*, 2883−2896.

(199) Burri, D. R.; Choi, K.-M.; Lee, J.-H.; Han, D.-S.; Park, S.-E. Influence of Sba-15 Support on Ceo2-Zro2 Catalyst for the Dehydrogenation of Ethylbenzene to Styrene with Co2. *Catal. Commun.* **2007**, *8*, 43−48.

(200) Grunewald, G.C.; Drago, R.S. Oxidative Dehydrogenation of Ethylbenzene to Styrene over Carbon-Based Catalysts. *J. Mol. Catal. A: Chem.* **1990**, *58*, 227−233.

(201) Pereira, M. F. R.; Figueiredo, J. L.; Órfão, J. J. M.; Serp, P.; Kalck, P.; Kihn, Y. Catalytic Activity of Carbon Nanotubes in the Oxidative Dehydrogenation of Ethylbenzene. *Carbon* **2004**, *42*, 2807−2813.

(202) Qui, N. V.; Scholz, P.; Krech, T.; Keller, T. F.; Pollok, K.; Ondruschka, B. Multiwalled Carbon Nanotubes Oxidized by Uv/H2o2 as Catalyst for Oxidative Dehydrogenation of Ethylbenzene. *Catal. Commun.* **2011**, *12*, 464−469.

(203) Diao, J.; Feng, Z.; Huang, R.; Liu, H.; Hamid, S. B.; Su, D. S. Selective and Stable Ethylbenzene Dehydrogenation to Styrene over Nanodiamonds under Oxygen-Lean Conditions. *ChemSusChem* **2016**, *9*, 662−666.

(204) Langeslay, R. R.; Kaphan, D. M.; Marshall, C. L.; Stair, P. C.; Sattelberger, A. P.; Delferro, M. Catalytic Applications of Vanadium: A Mechanistic Perspective. *Chem. Rev.* **2019**, *119*, 2128−2191.

(205) Pauly, T. R.; Pinnavaia, T. J. Pore Size Modification of Mesoporous Hms Molecularsieve Silicas with Wormhole Framework Structures. *Chem. Mater.* **2001**, *13*, 987−993.

(206) Jiang, N.; Burri, A.; Park, S.-E. Ethylbenzene to Styrene over Zro2-Based Mixed Metal Oxide Catalysts with Co2 as Soft Oxidant. *Chin. J. Catal.* **2016**, *37*, 3−15.

(207) Castro, A. J. R.; Soares, J. M.; Filho, J. M.; Oliveira, A. C.; Campos, A.; Milet, É. R. C. Oxidative Dehydrogenation of Ethylbenzene with Co2 for Styrene Production over Porous Iron-Based Catalysts. *Fuel* **2013**, *108*, 740−748.

(208) Wang, T.; Chong, S.; Wang, T.; Lu, H.; Ji, M. The Physicochemical Properties and Catalytic Performance of Carbon-Covered Alumina for Oxidative Dehydrogenation of Ethylbenzene with Co2. *Appl. Surf. Sci.* **2018**, *427*, 1011−1018.

(209) Fan, H.-X.; Feng, J.; Li, W.-Y.; Li, X.-H.; Wiltowski, T.; Ge, Q.-F. Role of Co2 in the Oxy-Dehydrogenation of Ethylbenzene to Styrene on the Ceo2(111) Surface. *Appl. Surf. Sci.* **2018**, *427*, 973−980.

(210) Mochalin, V. N.; Shenderova, O.; Ho, D.; Gogotsi, Y. The Properties and Applications of Nanodiamonds. *Nat. Nanotechnol.* **2012**, *7*, 11−23.

(211) Diao, J.; Zhang, Y.; Zhang, J.; Wang, J.; Liu, H.; Su, D. S. Fabrication of Mgo-Rgo Hybrid Catalysts with a Sandwich Structure for Enhanced Ethylbenzene Dehydrogenation Performance. *Chem. Commun. (Cambridge)* **2017**, *53*, 11322−11325.

(212) Hou, P.-X.; Liu, C.; Cheng, H.-M. Purification of Carbon Nanotubes. *Carbon* **2008**, *46*, 2003−2025.

(213) Qin, L.; Wang, L.; Wang, C.; Yang, X.; Lv, B. Enhanced Role of Graphitic-N on Nitrogen-Doped Porous Carbon Ball for Direct Dehydrogenation of Ethylbenzene. *Mol. Catal.* **2019**, *462*, 61−68.

(214) Zimmerman, J. L.; Bradley, R. K.; Huffman, C. B.; Hauge, R. H.; Margrave, J. L. Gas-Phase Purification of Single-Wall Carbon Nanotubes. *Chem. Mater.* **2000**, *12*, 1361−1366.

(215) Tobias, G.; Shao, L.; Salzmann, C. G.; Huh, Y.; Green, M. L. H. Purification and Opening of Carbon Nanotubes Using Steam. *J. Phys. Chem. B* **2006**, *110*, 22318−22322.

(216) Ajayan, P. M.; Ebbesen, T. W.; Ichihashi, T.; Iijima, S.; Tanigaki, K.; Hiura, H. Opening Carbon Nanotubes with Oxygen and Implications for Filling. *Nature* **1993**, *362*, 522−525.

(217) Zhang, J.; Zou, H.; Qing, Q.; Yang, Y.; Li, Q.; Liu, Z.; Guo, X.; Du, Z. Effect of Chemical Oxidation on the Structure of Single-Walled Carbon Nanotubes. *J. Phys. Chem. B* **2003**, *107*, 3712−3718.

(218) Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; et al. Smalley, Fullerene Pipes. *Science* **1998**, *280*, 1253−1256.

(219) Dujardin, E.; Ebbesen, T. W.; Krishnan, A.; Treacy, M. M. J. Purification of Single-Shell Nanotubes. *Adv. Mater.* **1998**, *10*, 611−613.

(220) Delgado, J. J.; Chen, X.; Tessonnier, J. P.; Schuster, M. E.; Del Rio, E.; Schlögl, R.; Su, D. S. Influence of the Microstructure of Carbon Nanotubes on the Oxidative Dehydrogenation of Ethylbenzene to Styrene. *Catal. Today* **2010**, *150*, 49−54.

(221) Lin, Y.; Sun, X.; Su, D. S.; Centi, G.; Perathoner, S. Catalysis by Hybrid Sp(2)/Sp(3) Nanodiamonds and Their Role in the Design of Advanced Nanocarbon Materials. *Chem. Soc. Rev.* **2018**, *47*, 8438−8473.

(222) Zhang, J.; Su, D. S.; Blume, R.; Schlogl, R.; Wang, R.; Yang, X.; Gajovic, A. Surface Chemistry and Catalytic Reactivity of a Nanodiamond in the Steam-Free Dehydrogenation of Ethylbenzene. *Angew. Chem., Int. Ed.* **2010**, *49*, 8640−4.

(223) Zhao, Z.; Dai, Y. Nanodiamond/Carbon Nitride Hybrid Nanoarchitecture as an Efficient Metal-Free Catalyst for Oxidant- and Steam-Free Dehydrogenation. *J. Mater. Chem. A* **2014**, *2*, 13442−13451.

(224) Feng, L.; Liu, Y.; Jiang, Q.; Liu, W.; Wu, K.-H.; Ba, H.; Pham-Huu, C.; Yang, W.; Su, D. S. Nanodiamonds @ N, P Co-Modified Mesoporous Carbon Supported on Macroscopic Sic Foam for Oxidative Dehydrogenation of Ethylbenzene. *Catal. Today* **2020**, *357*, 231−239.

(225) Zhou, Q.; Guo, X.; Song, C.; Zhao, Z. Defect-Enriched N,O-Codoped Nanodiamond/Carbon Nanotube Catalysts for Styrene Production Via Dehydrogenation of Ethylbenzene. *ACS Appl. Nano Mater.* **2019**, *2*, 2152−2159.

(226) Hauer, B. Embracing Nature's Catalysts: A Viewpoint on the Future of Biocatalysis. *ACS Catal.* **2020**, *10*, 8418−8427.

(227) Claypool, J. T.; Raman, D. R.; Jarboe, L. R.; Nielsen, D. R. Technoeconomic Evaluation of Bio-Based Styrene Production by Engineered Escherichia Coli. *J. Ind. Microbiol. Biotechnol.* **2014**, *41*, 1211−1216.

(228) Lian, J.; McKenna, R.; Rover, M. R.; Nielsen, D. R.; Wen, Z.; Jarboe, L. R. Production of Biorenewable Styrene: Utilization of Biomass-Derived Sugars and Insights into Toxicity. *J. Ind. Microbiol. Biotechnol.* **2016**, *43*, 595−604.

(229) McKenna, R.; Nielsen, D. R. Styrene Biosynthesis from Glucose by Engineered E. Coli. *Metab. Eng.* **2011**, *13*, 544−554.

(230) Liu, C.; Men, X.; Chen, H.; Li, M.; Ding, Z.; Chen, G.; Wang, F.; Liu, H.; Wang, Q.; Zhu, Y.; et al. A Systematic Optimization of Styrene Biosynthesis in Escherichia Coli Bl21(De3). *Biotechnol. Biofuels* **2018**, *11*, 14.

(231) McKenna, R.; Moya, L.; McDaniel, M.; Nielsen, D. R. Comparing in Situ Removal Strategies for Improving Styrene Bioproduction. *Bioproc. Biosyst. Eng.* **2015**, *38*, 165−174.

(232) Lee, K.; Bang, H. B.; Lee, Y. H.; Jeong, K. J. Enhanced Production of Styrene by Engineered Escherichia Coli and in Situ Product Recovery (Ispr) with an Organic Solvent. *Microb. Cell. Fact.* **2019**, *18*, 79.

(233) Grubbe, W. S.; Rasor, B. J.; Kruger, A.; Jewett, M. C.; Karim, A. S. Cell-Free Styrene Biosynthesis at High Titers. *Metab. Eng.* **2020**, *61*, 89−95.

(234) Easton, C. J.; Hutton, C. A. Synthesis of Each Stereoisomer of [3-*H,] Phenylalanine and Evaluation of the Stereochemical Course of the Reaction of (R)-Phenylalanine with (S) -Phenylalanine Ammonia-Lyase. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3545−3548.

(235) Pometto, A. L.; Crawford, D. L. Enzymatic Production of the Lignin Precursor Trans- [U-14 C]Cinnamic Acid from L-[U-14 C]Phenylalanine Using L-Phenylalanine Ammonia-Lyase. *Enzyme Microb. Technol.* **1981**, *3*, 73−75.

(236) Spekreijse, J.; Le Nôtre, J.; van Haveren, J.; Scott, E. L.; Sanders, J. P. M. Simultaneous Production of Biobased Styrene and Acrylates Using Ethenolysis. *Green Chem.* **2012**, *14*, 2747−2751.

(237) Chung, H.; Yang, J. E.; Ha, J. Y.; Chae, T. U.; Shin, J. H.; Gustavsson, M.; Lee, S. Y. Bio-Based Production of Monomers and Polymers by Metabolically Engineered Microorganisms. *Curr. Opin. Biotechnol.* **2015**, *36*, 73−84.

(238) Burdett, K. A.; Harris, L. D.; Margl, P.; Maughon, B. R.; Mokhtar-Zadeh, T.; Saucier, P. C.; Wasserman, E. P. Wasserman, Renewable Monomer Feedstocks Via Olefin Metathesis: Fundamental Mechanistic Studies of Methyl Oleate Ethenolysis with the First-Generation Grubbs Catalyst. *Organometallics* **2004**, *23*, 2027−2047.

(239) Marinescu, S. C.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. Hoveyda, Ethenolysis Reactions Catalyzed by Imido Alkylidene Monoaryloxide Monopyrrolide (Map) Complexes of Molybdenum. *J. American Chem. Soc.* **2009**, *131*, 10840−10841.

(240) Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. A General Model for Selectivity in Olefin Cross Metathesis. *J. American Chem. Soc.* **2003**, *125*, 11360−11370.

(241) van Schijndel, J.; Molendijk, D.; van Beurden, K.; Canalle, L. A.; Noël, T.; Meuldijk, J. Preparation of Bio-Based Styrene Alternatives and Their Free Radical Polymerization. *Eur. Polym. J.* **2020**, *125*, 109534.

(242) Yu, A. Z.; Serum, E. M.; Renner, A. C.; Sahouani, J. M.; Sibi, M. P.; Webster, D. C. Renewable Reactive Diluents as Practical Styrene Replacements in Biobased Vinyl Ester Thermosets. *ACS Sus. Chem. Eng.* **2018**, *6*, 12586−12592.

(243) Youngblood, J. P.; Sellars, A. B.; Clark, A. J.; Coles, S. R. Replacing Styrene with Bioderived Alternatives in Polyesters. *Green Mater.* **2015**, *3*, 35−42.

(244) Takeshima, H.; Satoh, K.; Kamigaito, M. Bio-Based Functional Styrene Monomers Derived from Naturally Occurring Ferulic Acid for Poly(Vinylcatechol) and Poly(Vinylguaiacol) Via Controlled Radical Polymerization. *Macromolecules* **2017**, *50*, 4206−4216.

(245) Takeshima, H.; Satoh, K.; Kamigaito, M. Scalable Synthesis of Bio-Based Functional Styrene: Protected Vinyl Catechol from Caffeic Acid and Controlled Radical and Anionic Polymerizations Thereof. *ACS Sus. Chem. Eng.* **2018**, *6*, 13681−13686.

(246) Fadlallah, S.; Sinha Roy, P.; Garnier, G.; Saito, K.; Allais, F. Are Lignin-Derived Monomers and Polymers Truly Sustainable? An in-Depth Green Metrics Calculations Approach. *Green Chem.* **2021**, *23*, 1495−1535.

(247) Finkle, B. J.; Lewis, J. C.; Corse, J. W.; Lundin, R. E. Enzyme Reactions with Phenolic Compounds: Formation of Hydroxystyrenes through the Decarboxylation of 4-Hydroxycinnamic Acids by Aerobacter. *J. Biol. Chem.* **1962**, *237*, 2926−2931.

(248) Nomura, E.; Hosoda, A.; Mori, H.; Taniguchi, H. Rapid Base-Catalyzed Decarboxylation and Amide-Forming Reaction of Substituted Cinnamic Acids Via Microwave Heating. *Green Chem.* **2005**, *7*, 863−866.

(249) Liu, D.; Sun, J.; Simmons, B. A.; Singh, S. N-Heterocyclic Carbene Promoted Decarboxylation of Lignin-Derived Aromatic Acids. *ACS Sus. Chem. Eng.* **2018**, *6*, 7232−7238.

(250) Cadot, S.; Rameau, N.; Mangematin, S.; Pinel, C.; Djakovitch, L. Preparation of Functional Styrenes from Biosourced Carboxylic Acids by Copper Catalyzed Decarboxylation in Peg. *Green Chem.* **2014**, *16*, 3089−3097.

(251) Nagai, K. New Developments in the Production of Methyl Methacrylate. *Appl. Catal. A: General* **2001**, *221*, 367−377.

(252) Darabi Mahboub, M. J.; Dubois, J. L.; Cavani, F.; Rostamizadeh, M.; Patience, G. S. Catalysis for the Synthesis of Methacrylic Acid and Methyl Methacrylate. *Chem. Soc. Rev.* **2018**, *47*, 7703−7738.

(253) Dubois, J.-L.; Croizy, J.-F. Biomass-Derived Methyl Methacrylate and Corresponding Manufacturing Method, Uses and Polymers. US 2011/0318515A1, 2011.

(254) Danner, H.; Urmos, M.; Gartner, M.; Braun, R. Biotechnological Production of Acrylic Acid from Biomass. *Appl. Microbiol. Biotechnol.* **1998**, *70-72*, 887−894.

(255) Zhang, J.; Lin, J.; Xu, X.; Cen, P. Evaluation of Catalysts and Optimization of Reaction Conditions for the Dehydration of Methyl Lactate to Acrylates. *Chin. J. Chem. Eng.* **2008**, *16*, 263−269.

(256) Gao, C.; Ma, C.; Xu, P. Biotechnological Routes Based on Lactic Acid Production from Biomass. *Biotechnol. Adv.* **2011**, *29*, 930−9.

(257) Corma, A.; Iborra, S.; Velty, A. Chemical Routes for the Transformation of Biomass into Chemicals. *Chem. Rev.* **2007**, *107*, 2411−2502.

(258) Shen, M.; Zheng, Y.-G.; Shen, Y.-C. Isolation and Characterization of a Novel Arthrobacter Nitroguajacolicus Zjutb06-99, Capable of Converting Acrylonitrile to Acrylic Acid. *Proc. Biochem.* **2009**, *44*, 781−785.

(259) Makshina, E. V.; Canadell, J.; van Krieken, J.; Peeters, E.; Dusselier, M.; Sels, B. F. Bio-Acrylates Production: Recent Catalytic Advances and Perspectives of the Use of Lactic Acid and Their Derivates. *ChemCatChem.* **2019**, *11*, 180−201.

(260) Beerthuis, R.; Rothenberg, G.; Shiju, N. R. Catalytic Routes Towards Acrylic Acid, Adipic Acid and E-Caprolactam Starting from Biorenewables. *Green Chem.* **2015**, *17*, 1341−1361.

(261) Jin, X.; Meng, K.; Zhang, G.; Liu, M.; Song, Y.; Song, Z.; Yang, C. Interfacial Catalysts for Sustainable Chemistry: Advances on Atom and Energy Efficient Glycerol Conversion to Acrylic Acid. *Green Chem.* **2021**, *23*, 51−76.

(262) Pirman, T.; Ocepek, M.; Likozar, B. Radical Polymerization of Acrylates, Methacrylates, and Styrene: Biobased Approaches, Mechanism, Kinetics, Secondary Reactions, and Modeling. *Ind. Eng. Chem. Res.* **2021**, *60*, 9347−9367.

(263) Li, X.; Zhang, Y. Oxidative Dehydration of Glycerol to Acrylic Acid over Vanadium-Substituted Cesium Salts of Keggin-Type Heteropolyacids. *ACS Catal.* **2016**, *6*, 2785−2791.

(264) Soriano, M. D.; Concepción, P.; Nieto, J. M. L.; Cavani, F.; Guidetti, S.; Trevisanut, C. Tungsten-Vanadium Mixed Oxides for the Oxidehydration of Glycerol into Acrylic Acid. *Green Chem.* **2011**, *13*, 2954−2962.

(265) Chieregato, A.; Basile, F.; Concepción, P.; Guidetti, S.; Liosi, G.; Soriano, M. D.; Trevisanut, C.; Cavani, F.; Nieto, J. M. L. Glycerol Oxidehydration into Acrolein and Acrylic Acid over W-V-Nb-O Bronzes with Hexagonal Structure. *Catal. Today* **2012**, *197*, 58−65.

(266) Yun, Y. S.; Lee, K. R.; Park, H.; Kim, T. Y.; Yun, D.; Han, J. W.; Yi, J. Rational Design of a Bifunctional Catalyst for the Oxydehydration of Glycerol: A Combined Theoretical and Experimental Study. *ACS Catal.* **2015**, *5*, 82−94.

(267) Chieregato, A.; Soriano, M. D.; Garcia-Gonzalez, E.; Puglia, G.; Basile, F.; Concepcion, P.; Bandinelli, C.; Lopez Nieto, J. M.; Cavani, F. Multielement Crystalline and Pseudocrystalline Oxides as Efficient Catalysts for the Direct Transformation of Glycerol into Acrylic Acid. *ChemSusChem* **2015**, *8*, 398−406.

(268) Chieregato, A.; Soriano, M. D.; Basile, F.; Liosi, G.; Zamora, S.; Concepción, P.; Cavani, F.; López Nieto, J. M. One-Pot Glycerol Oxidehydration to Acrylic Acid on Multifunctional Catalysts: Focus on the Influence of the Reaction Parameters in Respect to the Catalytic Performance. *Appl. Catal. B: Environ.* **2014**, *150-151*, 37−46.

(269) Omata, K.; Matsumoto, K.; Murayama, T.; Ueda, W. Direct Oxidative Transformation of Glycerol to Acrylic Acid over Nb-Based Complex Metal Oxide Catalysts. *Catal. Today* **2016**, *259*, 205−212.

(270) Sarkar, B.; Pendem, C.; Sivakumar Konathala, L. N.; Tiwari, R.; Sasaki, T.; Bal, R. Cu Nanoclusters Supported on Nanocrystalline Sio(2)-Mno(2): A Bifunctional Catalyst for the One-Step Conversion of Glycerol to Acrylic Acid. *Chem. Commun. (Cambridge)* **2014**, *50*, 9707−10.

(271) Thanasilp, S.; Schwank, J. W.; Meeyoo, V.; Pengpanich, S.; Hunsom, M. One-Pot Oxydehydration of Glycerol to Value-Added Compounds over Metal-Doped Siw/Hzsm-5 Catalysts: Effect of Metal Type and Loading. *Chem. Eng. J.* **2015**, *275*, 113−124.

(272) dos Santos, M. B.; Andrade, H. M. C.; Mascarenhas, A. J. S. Oxidative Dehydration of Glycerol over Alternative H,Fe-Mcm-22 Catalysts: Sustainable Production of Acrylic Acid. *Micropor. Mesopor. Mater.* **2019**, *278*, 366−377.

(273) Diallo, M. M.; Mijoin, J.; Laforge, S.; Pouilloux, Y. Preparation of Fe-Bea Zeolites by Isomorphous Substitution for Oxidehydration of Glycerol to Acrylic Acid. *Catal. Commun.* **2016**, *79*, 58−62.

(274) Haider, M. H.; Dummer, N. F.; Zhang, D.; Miedziak, P.; Davies, T. E.; Taylor, S. H.; Willock, D. J.; Knight, D. W.; Chadwick, D.; Hutchings, G. J. Rubidium- and Caesium-Doped Silicotungstic Acid Catalysts Supported on Alumina for the Catalytic Dehydration of Glycerol to Acrolein. *J. Catal.* **2012**, *286*, 206−213.

(275) Deleplanque, J.; Dubois, J. L.; Devaux, J. F.; Ueda, W. Production of Acrolein and Acrylic Acid through Dehydration and Oxydehydration of Glycerol with Mixed Oxide Catalysts. *Catal. Today* **2010**, *157*, 351−358.

(276) de Oliveira, A. S.; Vasconcelos, S. J. S.; de Sousa, J. R.; de Sousa, F. F.; Filho, J. M.; Oliveira, A. C. Catalytic Conversion of Glycerol to Acrolein over Modified Molecular Sieves: Activity and Deactivation Studies. *Chem. Eng. J.* **2011**, *168*, 765−774.

(277) Liu, R.; Wang, T.; Cai, D.; Jin, Y. Highly Efficient Production of Acrylic Acid by Sequential Dehydration and Oxidation of Glycerol. *Ind. Eng. Chem. Res.* **2014**, *53*, 8667−8674.

(278) Dubois, J.-L.; Duquenne, C.; Holderich, W. Method for Producing Acrylic Acid from Glycerol. US 7,910,771 B2, 2011.

(279) Lari, G. M.; Puértolas, B.; Frei, M. S.; Mondelli, C.; Pérez-Ramírez, J. Hierarchical Nay Zeolites for Lactic Acid Dehydration to Acrylic Acid. *ChemCatChem.* **2016**, *8*, 1507−1514.

(280) Sun, P.; Yu, D.; Tang, Z.; Li, H.; Huang, H. Nay Zeolites Catalyze Dehydration of Lactic Acid to Acrylic Acid: Studies on the Effects of Anions in Potassium Salts. *Ind. Eng. Chem. Res.* **2010**, *49*, 9082−9087.

(281) Sun, P.; Yu, D.; Fu, K.; Gu, M.; Wang, Y.; Huang, H.; Ying, H. Potassium Modified Nay: A Selective and Durable Catalyst for Dehydration of Lactic Acid to Acrylic Acid. *Catal. Commun.* **2009**, *10*, 1345−1349.

(282) Wang, H.; Yu, D.; Sun, P.; Yan, J.; Wang, Y.; Huang, H. Rare Earth Metal Modified Nay: Structure and Catalytic Performance for Lactic Acid Dehydration to Acrylic Acid. *Catal. Commun.* **2008**, *9*, 1799−1803.

(283) Yan, J.; Yu, D.; Li, H.; Sun, P.; Huang, H. Nay Zeolites Modified by La3+ and Ba2+: The Effect of Synthesis Details on Surface Structure and Catalytic Performance for Lactic Acid to Acrylic Acid. *J. Rare Earths* **2010**, *28*, 803−806.

(284) Yu, D.; Sun, P.; Tang, Z.; Li, Z.; Huang, H. Modification of Nay by La3+ for the Dehydration of Lactic Acid: The Effect of Preparation Protocol on Catalyst Microstructure and Catalytic Performance. *Canad. J. Chem. Eng.* **2011**, *89*, 484−490.

(285) Zhang, J.; Zhao, Y.; Pan, M.; Feng, X.; Ji, W.; Au, C.-T. Efficient Acrylic Acid Production through Bio Lactic Acid Dehydration over Nay Zeolite Modified by Alkali Phosphates. *ACS Catal.* **2011**, *1*, 32−41.

(286) Zhang, L.; Theng, D. S.; Du, Y.; Xi, S.; Huang, L.; Gao, F.; Wang, C.; Chen, L.; Borgna, A. Selective Conversion of Lactic Acid to Acrylic Acid over Alkali and Alkaline-Earth Metal Co-Modified Nay Zeolites. *Catal. Sci. Technol.* **2017**, *7*, 6101−6111.

(287) Yan, B.; Tao, L. Z.; Liang, Y.; Xu, B. Q. Sustainable Production of Acrylic Acid: Alkali-Ion Exchanged Beta Zeolite for Gas-Phase Dehydration of Lactic Acid. *ChemSusChem* **2014**, *7*, 1568−78.

(288) Yuan, C.; Liu, H.; Zhang, Z.; Lu, H.; Zhu, Q.; Chen, Y. Alkali-Metal-Modified Zsm-5 Zeolites for Improvement of Catalytic Dehydration of Lactic Acid to Acrylic Acid. *Chin. J. Catal.* **2015**, *36*, 1861−1866.

(289) Zhang, X.; Lin, L.; Zhang, T.; Liu, H.; Zhang, X. Catalytic Dehydration of Lactic Acid to Acrylic Acid over Modified Zsm-5 Catalysts. *Chem. Eng. J.* **2016**, *284*, 934−941.

(290) Jiang, B.; Li, Q.; Li, D.; Wang, W. Molecular Sieve Catalyst, Its Preparation Method and Application to Preparation of Acrylic Acid by Dehydration of Lactic Acid. CN 101602010, 2009.

(291) Zuo, S.; Zhang, J.; Liu, J. Preparation and Application of Catalyst Used in Production of Acrylic Acid through Dehydration of Lactic Acid. CN 102019193, 2011.

(292) Huang, H.; Shi, H.; Wang, H.; Yan, J..; Hu, Y.; Cheng, M.; Wang, Y.; Sun, P. Complex Type Molecular Sieve Catalysis, Preparation Method, and Application in Preparing Acrylic Acid. CN 1010495571, 2007.

(293) Ozmeral, C.; Dasari, R.; Singh, R.; Yu, N.; Rioux, R. M.; Roman-Leshkov, Y. Novel Method to Produce Acrylic Acid with Acetaldehyde as the Main by-Product. WO 2016/201181 A1, 2016.

(294) Näfe, G.; López-Martínez, M. A.; Dyballa, M.; Hunger, M.; Traa, Y.; Hirth, T.; Klemm, E. Deactivation Behavior of Alkali-Metal Zeolites in the Dehydration of Lactic Acid to Acrylic Acid. *J. Catal.* **2015**, *329*, 413−424.

(295) Ghantani, V. C.; Lomate, S. T.; Dongare, M. K.; Umbarkar, S. B. Catalytic Dehydration of Lactic Acid to Acrylic Acid Using Calcium Hydroxyapatite Catalysts. *Green Chem.* **2013**, *15*, 1211−1217.

(296) Yan, B.; Tao, L.-Z.; Liang, Y.; Xu, B.-Q. Sustainable Production of Acrylic Acid: Catalytic Performance of Hydroxyapatites for Gas-Phase Dehydration of Lactic Acid. *ACS Catal.* **2014**, *4*, 1931−1943.

(297) Matsuura, Y.; Onda, A.; Yanagisawa, K. Selective Conversion of Lactic Acid into Acrylic Acid over Hydroxyapatite Catalysts. *Catal. Commun.* **2014**, *48*, 5−10.

(298) Ghantani, V. C.; Dongare, M. K.; Umbarkar, S. B. Nonstoichiometric Calcium Pyrophosphate: A Highly Efficient and Selective Catalyst for Dehydration of Lactic Acid to Acrylic Acid. *RSC Adv.* **2014**, *4*, 33319−33326.

(299) Lingoes, J. V.; Collias, D. I. Catalytic Conversion of Lactic Acid to Acrylic Acid Using Mixed Phosphate Catalyst. WO 2013/155245, 2013.

(300) Lingoes, J. V.; Collias, D. I. Catalytic Conversion of Lactic Acid to Acrylic Acid. US 2013/0274514 A1, 2013.

(301) Tang, C.; Peng, J.; Li, X.; Zhai, Z.; Jiang, N.; Bai, W.; Gao, H.; Liao, Y. Strontium Pyrophosphate Modified by Phosphoric Acid for the Dehydration of Lactic Acid to Acrylic Acid. *RSC Adv.* **2014**, *4*, 28875−28882.

(302) Tang, C.; Peng, J.; Fan, G.; Li, X.; Pu, X.; Bai, W. Catalytic Dehydration of Lactic Acid to Acrylic Acid over Dibarium Pyrophosphate. *Catal. Commun.* **2014**, *43*, 231−234.

(303) Peng, J.; Li, X.; Tang, C.; Bai, W. Barium Sulphate Catalyzed Dehydration of Lactic Acid to Acrylic Acid. *Green Chem.* **2014**, *16*, 108−111.

(304) Nagaraju, N.; Kumar, V. P.; Srikanth, A.; Rajan, N. P.; Chary, K. V. R. Vapor-Phase Catalytic Dehydration of Lactic Acid to Acrylic Acid over Nano-Crystalline Cerium Phosphate Catalysts. *Appl. Petrochem. Res.* **2016**, *6*, 367−377.

(305) Guo, Z.; Theng, D. S.; Tang, K. Y.; Zhang, L.; Huang, L.; Borgna, A.; Wang, C. Dehydration of Lactic Acid to Acrylic Acid over Lanthanum Phosphate Catalysts: The Role of Lewis Acid Sites. *Phys. Chem. Chem. Phys.* **2016**, *18*, 23746−23754.

(306) Redmon, B. C. Preparation of Acrylic Acid. US 2469701, 1946.

(307) Redmon, B. C.; Griffin, G. R. Preparation of Esters of Acrylic Acid. US 246768, 1946.

(308) Tsobanakis, P. M. X.; Abraham, T. W. Methods of Manufacturing Derivatives of Β-Hydroxycarboxylic Acids. WO 2003082795, 2003.

(309) Craciun, L.; Benn, G. P.; Dewing, J.; Schriver, G. W.; Peer, W. J.; Siebenhaar, B.; Siegrist, U. Preparation of Acrylic Acid Derivatives from Alpha-or Beta-Hydroxy Carboxylic Acids. US 2005222458, 2005.

(310) Tsobanakis, P.; Meng, X. M.; Abraham, T. W. Methods of Manufacturing Derivatives of Β-Hydroxycarboxylic Acids. WO 03/082795, 2003.

(311) Cracium, L.; Benn, G. P.; Dewing, J.; Schriver, G. W.; Peer, W. J.; Siebenhaar, B.; Siegrist, U. Preparation of Acrylic Acid from a- or Β- Hydroxy Carboxylic Acids. US 7538247 B2, 2009.

(312) Holladay, J. E.; Zacher, A. H.; Lilga, M. A.; White, J. F.; Muzatko, D. S.; Orth, R. J.; Tsobanakis, P.; Meng, X.; Abraham, T. W. Method for the Preparation of Alpha-Beta-Unsaturated Carbonyl Compounds. WO 2007106099, 2007.

(313) Lilga, M. A.; White, J. F.; Holladay, J. E.; Zacher, A. H.; Muzatko, D. S.; Orth, R. J. Method for Conversion of Beta-Hydroxy Carbonyl Compounds. US 2007/0219391 A1, 2007.

(314) Li, C.; Zhu, Q.; Cui, Z.; Wang, B.; Fang, Y.; Tan, T. Highly Efficient and Selective Production of Acrylic Acid from 3-Hydroxypropionic Acid over Acidic Heterogeneous Catalysts. *Chem. Eng. Sci.* **2018**, *183*, 288−294.

(315) Tengler, R.; Decoster, D.; Hoyt, S.; Roach, S. Purification of 3-Hydroxypropionic Acid from Crude Cell Broth and Dehydration to Acrylic Acid. WO 2013/192453, 2013.

(316) Chwae, J.; Park, N. S.; Lee, M. H.; Kim, J. W. Preparation of Unsaturated Carboxylic Acids from Hydroxycarboxylic Acids. US 2014/0171681, 2014.

(317) Murayama, T.; Katryniok, B.; Heyte, S.; Araque, M.; Ishikawa, S.; Dumeignil, F.; Paul, S.; Ueda, W. Role of Crystalline Structure in Allyl Alcohol Selective Oxidation over Mo3vox Complex Metal Oxide Catalysts. *ChemCatChem.* **2016**, *8*, 2415−2420.

(318) Ishikawa, S.; Murayama, T.; Katryniok, B.; Dumeignil, F.; Araque, M.; Heyte, S.; Paul, S.; Yamada, Y.; Iwazaki, M.; Noda, N.; et al. Influence of the Structure of Trigonal Mo-V-M3rd Oxides (M3rd = -, Fe, Cu, W) on Catalytic Performances in Selective Oxidations of Ethane, Acrolein, and Allyl Alcohol. *Appl. Catal. A: General* **2019**, *584*, 117151.

(319) Yang, S.; Kim, M.; Yang, S.; Kim, D. S.; Lee, W. J.; Lee, H. Production of Acrylic Acid from Biomass-Derived Allyl Alcohol by

Selective Oxidation Using Au/Ceria Catalysts. *Catal. Sci. Technol.* **2016**, *6*, 3616−3622.

(320) Kim, M.; Lee, H. Highly Selective Production of Acrylic Acid from Glycerol Via Two Steps Using Au/Ceo2 Catalysts. *ACS Sus. Chem. Eng.* **2017**, *5*, 11371−11376.

(321) Kim, M.; Lee, H. Selective Oxidation of Allyl Alcohol to Acrylic Acid in Base-Free Aqueous Solution. *ChemistrySelect* **2017**, *2*, 2420−2425.

(322) Bae, J.-W.; Potdar, H. S.; Kang, S.-H.; Jun, K.-W. Coproduction of Methanol and Dimethyl Ether from Biomass-Derived Syngas on a Cu-Zno-Al2o3/Γ-Al2o3 Hybrid Catalyst. *Energy Fuels* **2008**, *22*, 223−230.

(323) Németh, Á.; Vidra, A. Bio-Produced Acetic Acid: A Review. *Perio. Polytech. Chem. Eng.* **2018**, *62*, 245−256.

(324) Hu, J.; Lu, Z.; Yin, H.; Xue, W.; Wang, A.; Shen, L.; Liu, S. Aldol Condensation of Acetic Acid with Formaldehyde to Acrylic Acid over Sio2-, Sba-15-, and Hzsm-5-Supported V-P-O Catalysts. *J. Ind. Eng. Chem.* **2016**, *40*, 145−151.

(325) Wang, A.; Hu, J.; Yin, H.; Lu, Z.; Xue, W.; Shen, L.; Liu, S. Aldol Condensation of Acetic Acid with Formaldehyde to Acrylic Acid over Cs(Ce, Nd) Vpo/Sio2 Catalyst. *RSC Adv.* **2017**, *7*, 48475−48485.

(326) Liu, J.; Xu, P.; Wang, P.; Xu, Z.; Feng, X.; Ji, W.; Au, C. T. Vanadium Phosphorus Oxide/Siliceous Mesostructured Cellular Foams: Efficient and Selective for Sustainable Acrylic Acid Production Via Condensation Route. *Sci. Rep.* **2019**, *9*, 16988.

(327) van Leeuwen, B. N.; van der Wulp, A. M.; Duijnstee, I.; van Maris, A. J.; Straathof, A. J. Fermentative Production of Isobutene. *Appl. Microbiol. Biotechnol.* **2012**, *93*, 1377−87.

(328) Mizuno, N.; Yahiro, H. Oxidation of Isobutane Catalyzed by Partially Salified Cesium Molybdovanadophosphoric Acids. *J. Phys. Chem. B* **1998**, *102*, 437−443.

(329) Li, W.; Ueda, W. Catalytic Oxidation of Isobutane to Methacrylic Acid with Molecular Oxygen over Activated Pyridinium 12-Molybdophosphate. *Catal. Lett.* **1997**, *46*, 261−265.

(330) Mizuno, N.; Tateishi, M.; Iwamoto, M. Oxidation of Isobutane Catalyzed by Csxh3Xpmo12o40-Based Heteropoly Compounds. *J. Catal.* **1996**, *163*, 87−94.

(331) Cavani, F.; Mezzogori, R.; Pigamo, A.; Trifiro, F. Synthesis of methacrylic acid by selective oxidation of isobutane, catalysed by Keggin-type polyoxometalates: relationship between catalytic performance, reaction conditions and chemical−physical features of the catalyst. *C. R. Acad. Sci., Ser. IIc: Chim.* **2000**, *3*, 523−531.

(332) Wu, S.; Kan, Q.; Ding, W.; Shang, F.; Liu, H.; Guan, J. Partial Oxidation of Isobutane to Methacrolein over Te(1.5+0.5x)Pmo12-Xvxon Heteropolycompounds with Tellurium as Counter Cations. *React. Kinet. Mech. Catal.* **2012**, *106*, 157−164.

(333) Liu-Cai, F. X.; Pham, C.; Bey, F.; Herve, G. Oxidation of Isobutane Catalyzed by Vanadyl Copper and Cesium Substituted H3pmo12o40. *React. Kinet. Catal. Lett.* **2002**, *75*, 305−314.

(334) He, J.; Liu, Y.; Chu, W.; Yang, W. Effect of V-Containing Precursors on the Structure and Catalytic Performance of Cs-Substituted Phosphomolybdates for Isobutane Oxidation. *Appl. Catal. A: General* **2018**, *556*, 104−112.

(335) Jing, F.; Katryniok, B.; Dumeignil, F.; Bordes-Richard, E.; Paul, S. Catalytic Selective Oxidation of Isobutane over Csx(Nh4)3-Xhpmo11vo40mixed Salts. *Catal. Sci. Technol.* **2014**, *4*, 2938−2945.

(336) Jing, F.; Katryniok, B.; Dumeignil, F.; Bordes-Richard, E.; Paul, S. Catalytic Selective Oxidation of Isobutane to Methacrylic Acid on Supported (Nh4)3hpmo11vo40 Catalysts. *J. Catal.* **2014**, *309*, 121−135.

(337) Liu, Y.; He, J.; Chu, W.; Yang, W. Polyoxometalate Catalysts with Co-Substituted Vo2+ and Transition Metals and Their Catalytic Performance for the Oxidation of Isobutane. *Catal. Sci. Technol.* **2018**, *8*, 5774−5781.

(338) Mizuno, N.; Tateishi, M.; Iwamoto, M. Direct Oxidation of Lsobutane into Methacrylic Acid and Methacrolein over Cs2.5ni0.08-Substituted Hd3pmo12o40. *J. Chem. Soc., Chem. Commun.* **1994**, 1411−1412.

(339) Guan, J.; Wu, S.; Wang, H.; Jing, S.; Wang, G.; Zhen, K.; Kan, Q. Synthesis and Characterization of Movteceo Catalysts and Their Catalytic Performance for Selective Oxidation of Isobutane and Isobutylene. *J. Catal.* **2007**, *251*, 354−362.

(340) Guan, J.; Wang, H.; Song, K.; Xu, C.; Wang, Z.; Kan, Q. Selective Oxidation of Isobutane over Hydrothermally Synthesized Mo-V-Te-Sb-O Mixed Oxide Catalysts. *Catal. Commun.* **2009**, *10*, 1437−1440.

(341) Carlsson, M.; Habenicht, C.; Kam, L. C.; Antal, M. J., Jr.; Bian, N.; Cunningham, R. J.; Jones, M., Jr. Study of the Sequential Conversion of Citric to Itaconic to Methacrylic Acid in near-Critical and Supercritical Water. *Ind. Eng. Chem. Res.* **1994**, *33*, 1989−1996.

(342) Li, J.; Brill, T. B. Spectroscopy of Hydrothermal Solutions 18: Ph-Dependent Kinetics of Itaconic Acid Reactions in Real Time. *J. Phys. Chem. A* **2001**, *105*, 10839−10845.

(343) Eastham, G. R.; Johnson, D. W.; Waugh, M. Process for the Production of Methacrylic Acid and Its Derivatives and Polymers Produced Therefrom. US 2015/0094438A1, 2015.

(344) Lansing, J. C.; Murray, R. E.; Moser, B. R. Biobased Methacrylic Acid Via Selective Catalytic Decarboxylation of Itaconic Acid. *ACS Sus. Chem. Eng.* **2017**, *5*, 3132−3140.

(345) Le Notre, J.; Witte-van Dijk, S. C.; van Haveren, J.; Scott, E. L.; Sanders, J. P. Synthesis of Bio-Based Methacrylic Acid by Decarboxylation of Itaconic Acid and Citric Acid Catalyzed by Solid Transition-Metal Catalysts. *ChemSusChem* **2014**, *7*, 2712−20.

(346) Bohre, A.; Ali, M. A.; Ocepek, M.; Grilc, M.; Zabret, J.; Likozar, B. Copolymerization of Biomass-Derived Carboxylic Acids for Biobased Acrylic Emulsions. *Ind. Eng. Chem. Res.* **2019**, *58*, 19825−19831.

(347) Pirmoradi, M.; Kastner, J. R. Synthesis of Methacrylic Acid by Catalytic Decarboxylation and Dehydration of Carboxylic Acids Using a Solid Base and Subcritical Water. *ACS Sus. Chem. Eng.* **2017**, *5*, 1517−1527.

(348) Bohre, A.; Hočevar, B.; Grilc, M.; Likozar, B. Selective Catalytic Decarboxylation of Biomass-Derived Carboxylic Acids to Bio-Based Methacrylic Acid over Hexaaluminate Catalysts. *Appl. Catal. B: Environ.* **2019**, *256*, 117889.

(349) Chakraborti, A. K.; Patel, A. R.; Kumar, D.; Bindal, S. Process for Esterification of Carboxylic Acids with Organic Carbonates Catalyzed by Metal Lewis Acids. IN 2009DE01046, 2010.

(350) Selva, M.; Perosa, A. Green Chemistry Metrics: A Comparative Evaluation of Dimethyl Carbonate, Methyl Iodide, Dimethyl Sulfate and Methanol as Methylating Agents. *Green Chem.* **2008**, *10*, 457−464.

(351) Sun, H.-B.; Hua, R.; Yin, Y. Zrocl2·8h2o: An Efficient, Cheap and Reusable Catalyst for the Esterification of Acrylic Acid and Other Carboxylic Acids with Equimolar Amounts of Alcohols. *Molecules* **2006**, *11*, 263−271.

(352) Wasewar, K. L.; Yawalkar, A. A.; Moulijn, J. A.; Pangarkar, V. G. Fermentation of Glucose to Lactic Acid Coupled with Reactive Extraction: A Review. *Ind. Eng. Chem. Res.* **2004**, *43*, 5969−5982.

(353) Min-tian, G.; Hirata, M.; Koide, M.; Takanashi, H.; Hano, T. Production of L-Lactic Acid by Electrodialysis Fermentation (Edf). *Proc. Biochem.* **2004**, *39*, 1903−1907.

(354) Onda, A.; Matsuura, Y.; Yanagisawa, K. Method for Synthesizing Unsaturated Carboxylic Acid and/or Derivative of Same. US 2012/0277467, 2012.

(355) Onda, A.; Matsuura, Y.; Yanagisawa, K. Kubo Synthesis Catalyst and Synthesis Method for Unsaturated Carboxylic Acid and/or Derivative Thereof. US 2016/0096166, 2016.

(356) Hong, J.-h.; Han, Y.-h.; Kim, H.-r.; Jang, J.-s. Preparation of Calcium Phosphate Dehydration Catalyst for Preparation of Acrylic Acid and Acrylates from Lactates. KR 2012025888, 2012.

(357) Hong, J. H.; Lee, J.-M.; Kim, H.; Hwang, Y. K.; Chang, J.-S.; Halligudi, S. B.; Han, Y.-H. Efficient and Selective Conversion of Methyl Lactate to Acrylic Acid Using Ca3(Po4)2-Ca2(P2o7) Composite Catalysts. *Appl. Catal. A: General* **2011**, *396*, 194−200.

(358) Walkup, P. C.; Rohrmann, C. A.; Hallen, R. T.; Eakin, D. E. Production of Esters of Lactic Acid, Esters of Acrylic Acid, Lactic Acid, and Acrylic Acid. US 5252473, 1993.

(359) Walkup, P. C.; Rohrmann, C. A.; Hallen, R. T.; Eakin, D. E. Production of Esters of Lactic Acid, Esters of Acrylic Acid, Lactic Acid, and Acrylic Acid. US 5071754, 1991.

(360) Abe, T.; Hieda, S. Process for Preparing Unsaturated Carboxylic Acid or Ester Thereof. US 5250729, 1993.

(361) Abe, T.; Hieda, S. Process for Preparing Unsaturated Carboxylic Acid or Ester Thereof. EP 0379691, 1990.

(362) Ozmeral, C.; Glas, J. P.; Dasari, R.; Tanielyan, S.; Bhagat, R. D.; Kasireddy, M. R. Catalytic Dehydration of Lactic Acid and Lactic Acid Esters. WO 2012/033845, 2012.

(363) Bai, T.; Li, J.; Zuo, S.; Liu, J. Method for Preparation of Acrylate Via Catalytic Dehydration of Lactate. CN 102001942, 2011.

(364) Bensabeh, N.; Ronda, J. C.; Galia, M.; Cadiz, V.; Lligadas, G.; Percec, V. Set-Lrp of the Hydrophobic Biobased Menthyl Acrylate. *Biomacromolecules* **2018**, *19*, 1256−1268.

(365) Veith, C.; Diot-Néant, F.; Miller, S. A.; Allais, F. Synthesis and Polymerization of Bio-Based Acrylates: A Review. *Polym. Chem.* **2020**, *11*, 7452−7470.

(366) Hasegawa, S.; Azuma, M.; Takahashi, K. Stabilization of Enzyme Activity During the Esterification of Lactic Acid in Hydrophobic Ethers and Ketones as Reaction Media That Are Miscible with Lactic Acid Despite Their High Hydrophobicity. *Enzyme Microb. Technol.* **2008**, *43*, 309−316.

(367) Waghmare, A. A.; Hindupur, R. M.; Pati, H. N. Propylphosphonic Anhydride (T3p®): An Expedient Reagent for Organic Synthesis. *Rev. J. Chem.* **2014**, *4*, 53−131.

(368) Purushothaman, M.; Krishnan, P. S. G.; Nayak, S. K. Poly(Alkyl Lactate Acrylate)S Having Tunable Hydrophilicity. *J. Appl. Polym. Sci.* **2014**, *131*, 40962.

(369) Pham, P. D.; Monge, S.; Lapinte, V.; Raoul, Y.; Robin, J. J. Glycerol-Based Co-Oligomers by Free-Radical Chain Transfer Polymerization: Towards Reactive Polymers Bearing Acetal and/or Carbonate Groups with Enhanced Properties. *Eur. Polym. J.* **2017**, *95*, 491−502.

(370) Goyal, S.; Lin, F.-Y.; Forrester, M.; Henrichsen, W.; Murphy, G.; Shen, L.; Wang, T.-p.; Cochran, E. W. Glycerol Ketals as Building Blocks for a New Class of Biobased (Meth)Acrylate Polymers. *ACS Sus. Chem. Eng.* **2021**, *9*, 10620−10629.

(371) Yu, D. M.; Smith, D. M.; Kim, H.; Mapas, J. K. D.; Rzayev, J.; Russell, T. P. Morphological Evolution of Poly(Solketal Methacrylate)-Block-Polystyrene Copolymers in Thin Films. *Macromolecules* **2019**, *52*, 3592−3600.

(372) Zhang, D.; Zhang, H.; Nie, J.; Yang, J. Synthesis and Self-Assembly Behavior of Ph-Responsive Amphiphilic Copolymers Containing Ketal Functional Groups. *Polym. Internat.* **2010**, *59*, 967−974.

(373) Rossi, N. A. A.; Zou, Y.; Scott, M. D.; Kizhakkedathu, J. N. Raft Synthesis of Acrylic Copolymers Containing Poly(Ethylene Glycol) and Dioxolane Functional Groups: Toward Well-Defined Aldehyde Containing Copolymers for Bioconjugation. *Macromolecules* **2008**, *41*, 5272−5282.

(374) Oguchi, K.; Sanui, K.; Ogata, N.; Takahashi, Y.; Nakada, T. Relationship between Electron Sensitivity and Chemical Structures of Polymers as Electron Beam Resist. Vii: Electron Sensitivity of Vinyl Polymers Containing Pendant 1,3=Dioxolan Groups. *Polym. Eng. Sci.* **1990**, *30*, 449−452.

(375) Cai-Yuan, P.; Lei, T.; De-Cheng, W. Synthesis and Characterizations of the Four-Armed Amphiphilic Block Copolymer S[Poly(2,3-Dihydroxypropyl Acrylate)-Block-Poly(Methyl Acrylate)]-4. *J. Polym. Sci. A: Polym. Chem.* **2001**, *39*, 3062−3072.

(376) Beyaz, K.; Vaca-Garcia, C.; Vedrenne, E.; Haddadine, N.; Benaboura, A.; Thiebaud-Roux, S. Graft Copolymerization of Hydroxyethyl Cellulose with Solketal Acrylate: Preparation and Characterization for Moisture Absorption Application. *Int. J. Polym. Anal.* **2019**, *24*, 245−256.

(377) Beyaz, K.; Charton, M.; Rouilly, A.; Vedrenne, E.; Vaca-Garcia, C.; Benaboura, A.; Thiebaud-Roux, S. Synthesis of Graft -Copolymers from Palm Cellulose and Solketal Acrylate and Their Characterization. *Ind. Crops Prod.* **2017**, *97*, 32−40.

(378) Yu, X.; Picker, M.-T.; Schneider, M.; Herberg, A.; Pascual, S.; Fontaine, L.; Kuckling, D. Synthesis of Amphiphilic Block Copolymers Based on Ska by Raft Polymerization. *Macromol. Chem. Phys.* **2018**, *219*, 1700506.

(379) Louage, B.; Zhang, Q.; Vanparijs, N.; Voorhaar, L.; Vande Casteele, S.; Shi, Y.; Hennink, W. E.; Van Bocxlaer, J.; Hoogenboom, R.; De Geest, B. G. Degradable Ketal-Based Block Copolymer Nanoparticles for Anticancer Drug Delivery: A Systematic Evaluation. *Biomacromolecules* **2015**, *16*, 336−50.

(380) Zhang, Q.; Hou, Z.; Louage, B.; Zhou, D.; Vanparijs, N.; De Geest, B. G.; Hoogenboom, R. Acid-Labile Thermoresponsive Copolymers That Combine Fast Ph-Triggered Hydrolysis and High Stability under Neutral Conditions. *Angew. Chem., Int. Ed.* **2015**, *54*, 10879−83.

(381) Kenjo, S.; Yoshitake, H. Alkoxylation of A, B-Unsaturated Aldehydes on Gold Supported on Mesoporous Anatase. *Micropor. Mesopor. Mater.* **2017**, *237*, 12−22.

(382) Tsutsumi, K.; Yoshitake, H. Coupling Reaction between A,B-Unsaturated Aldehyde and Methanol Catalysed by Gold-Supported on Mesostructured Cerias. *Appl. Catal. A: General* **2014**, *484*, 64−73.

(383) Marsden, C.; Taarning, E.; Hansen, D.; Johansen, L.; Klitgaard, S. K.; Egeblad, K.; Christensen, C. H. Aerobic Oxidation of Aldehydes under Ambient Conditions Using Supported Gold Nanoparticle Catalysts. *Green Chem.* **2008**, *10*, 168−170.

(384) AI, M. Vapor-Phase Aldol Condensation of Formaldehyde with Acetic Acid on V205-P205 Catalysts. *J. Catal.* **1987**, *107*, 201−208.

(385) Zhao, H.; Zuo, C.; Yang, D.; Li, C.; Zhang, S. Effects of Support for Vanadium Phosphorus Oxide Catalysts on Vapor-Phase Aldol Condensation of Methyl Acetate with Formaldehyde. *Ind. Eng. Chem. Res.* **2016**, *55*, 12693−12702.

(386) Yan, J.; Zhang, C.; Ning, C.; Tang, Y.; Zhang, Y.; Chen, L.; Gao, S.; Wang, Z.; Zhang, W. Vapor Phase Condensation of Methyl Acetate with Formaldehyde to Preparing Methyl Acrylate over Cesium Supported Sba-15 Catalyst. *J. Ind. Eng. Chem.* **2015**, *25*, 344−351.

(387) Zuo, C.; Ge, T.; Guo, X.; Li, C.; Zhang, S. Synthesis and Catalytic Performance of Cs/P Modified Zsm-5 Zeolite in Aldol Condensation of Methyl Acetate with Different Sources of Formaldehyde. *Micropor. Mesopor. Mater.* **2018**, *256*, 58−66.

(388) Lomege, J.; Lapinte, V.; Negrell, C.; Robin, J. J.; Caillol, S. Fatty Acid-Based Radically Polymerizable Monomers: From Novel Poly(Meth)Acrylates to Cutting-Edge Properties. *Biomacromolecules* **2019**, *20*, 4−26.

(389) Guit, J.; Tavares, M. B. L.; Hul, J.; Ye, C.; Loos, K.; Jager, J.; Folkersma, R.; Voet, V. S. D. Photopolymer Resins with Biobased Methacrylates Based on Soybean Oil for Stereolithography. *ACS Appl. Polym. Mater.* **2020**, *2*, 949−957.

(390) Meng, L.; Qiu, H.; Wang, D.; Feng, B.; Di, M.; Shi, J.; Wei, S. Castor-Oil-Based Waterborne Acrylate/Sio2 Hybrid Coatings Prepared Via Sol-Gel and Thiol-Ene Reactions. *Prog. Org. Coat.* **2020**, *140*, 105492.

(391) Ecochard, Y.; Auvergne, R.; Boutevin, B.; Caillol, S. Linseed Oil-Based Thermosets by Aza-Michael Polymerization. *Eur. J. Lipid Sci. Technol.* **2020**, *122*, 1900145−1900153.

(392) Kai Ling, C.; Aung, M. M.; Rayung, M.; Chuah Abdullah, L.; Lim, H. N.; Mohd Noor, I. S. Performance of Ionic Transport Properties in Vegetable Oil-Based Polyurethane Acrylate Gel Polymer Electrolyte. *ACS Omega* **2019**, *4*, 2554−2564.

(393) Wu, Q.; Hu, Y.; Tang, J.; Zhang, J.; Wang, C.; Shang, Q.; Feng, G.; Liu, C.; Zhou, Y.; Lei, W. High-Performance Soybean-Oil-Based Epoxy Acrylate Resins: "Green" Synthesis and Application in Uv-Curable Coatings. *ACS Sus. Chem. Eng.* **2018**, *6*, 8340−8349.

(394) Badía, A.; Movellan, J.; Barandiaran, M. J.; Leiza, J. R. High Biobased Content Latexes for Development of Sustainable Pressure Sensitive Adhesives. *Ind. Eng. Chem. Res.* **2018**, *57*, 14509−14516.

(395) Sánchez, M. A.; Torres, G. C.; Mazzieri, V. A.; Pieck, C. L. Selective Hydrogenation of Fatty Acids and Methyl Esters of Fatty Acids to Obtain Fatty Alcohols-a Review. *J. Chem. Technol. Biotechnol.* **2017**, *92*, 27−42.

(396) Khalkar, S.; Bhowmick, D.; Pratap, A. Synthesis of Polymers from Fatty Alcohol and Acrylic Acid and Its Impact on Tribological Properties. *J. Oleo. Sci.* **2013**, *62*, 167−173.

(397) Soldi, R. A.; Oliveira, A. R. S.; Barbosa, R. V.; César-Oliveira, M. A. F. Polymethacrylates: Pour Point Depressants in Diesel Oil. *Eur. Polym. J.* **2007**, *43*, 3671−3678.

(398) Warwel, S.; Steinke, G.; Klaas, M. R. An Efficient Method for Lipase-Catalysed Preparation of Acrylic and Ethacrylic Acid Ester. *Biotechnol. Tech.* **1996**, *10*, 283−286.

(399) Chen, F.-B.; Bufkin, B. G. Crosslinkable Emulsion Polymers by Autoxidation. I. Reactivity Ratios. *J. Appl. Polym. Sci.* **1985**, *30*, 4571−4582.

(400) Çayli, G.; Meier, M. A. R. Polymers from Renewable Resources: Bulk Atrp of Fatty Alcohol-Derived Methacrylates. *Eur. J. Lipid Sci. Technol.* **2008**, *110*, 853−859.

(401) Campanella, A.; La Scala, J. J.; Wool, R. P. The Use of Acrylated Fatty Acid Methyl Esters as Styrene Replacements in Triglyceride-Based Thermosetting Polymers. *Polym. Eng. Sci.* **2009**, *49*, 2384−2392.

(402) Medeiros, A. M. M. S.; Machado, F.; Rubim, J. C.; McKenna, T. F. L. Bio-Based Copolymers Obtained through Miniemulsion Copolymerization of Methyl Esters of Acrylated Fatty Acids and Styrene. *J. Polym. Sci. A: Polym. Chem.* **2017**, *55*, 1422−1432.

(403) Saithai, P.; Lecomte, J.; Dubreucq, E.; Tanrattanakul, V. Effects of Different Epoxidation Methods of Soybean Oil on the Characteristics of Acrylated Epoxidized Soybean Oil-Co Poly(Methyl Methacrylate) Copolymer. *Express Polym. Lett.* **2013**, *7*, 910−924.

(404) Bunker, S.; Staller, C.; Willenbacher, N.; Wool, R. Miniemulsion Polymerization of Acrylated Methyl Oleate for Pressure Sensitive Adhesives. *Int. J. Adhes. Adhes.* **2003**, *23*, 29−38.

(405) Klapperich, C. M.; Noack, C. L.; Kaufman, J. D.; Zhu, L.; Bonnaillie, L.; Wool, R. P. A Novel Biocompatible Adhesive Incorporating Plant-Derived Monomers. *J. Biomed. Mater. Res., Part A* **2009**, *91*, 378−384.

(406) Tang, Q.; Li, Q.; Luo, Y.; Pan, X.; Xi, Z.; Zhao, L. Development of an Innovative Biobased Uv Coating Synthesized from Acrylated Epoxidized Soybean Oil and Poly(Octamethylene Maleate (Anhydride) Citrate). *Ind. Eng. Chem. Res.* **2021**, *60*, 9797−9806.

(407) Walther, S.; Strehmel, N.; Schlorholz, M.; Strehmel, B.; Strehmel, V. Photopolymerisation of Functionalised Monomers Derived from Oleic Acid. *J. Photopolym. Sci. Technol.* **2016**, *29*, 123−132.

(408) Huang, Y.-B.; Yao, M.-Y.; Xin, P.-P.; Zhou, M.-C.; Yang, T.; Pan, H. Influence of Alkenyl Structures on the Epoxidation of Unsaturated Fatty Acid Methyl Esters and Vegetable Oils. *RSC Adv.* **2015**, *5*, 74783−74789.

(409) Pelletier, H.; Belgacem, N.; Gandini, A. Acrylated Vegetable Oils as Photocrosslinkable Materials. *J. Appl. Polym. Sci.* **2006**, *99*, 3218−3221.

(410) Eren, T.; Küsefoğlu, S. H. One Step Hydroxybromination of Fatty Acid Derivatives. *Eur. J. Lipid Sci. Technol.* **2004**, *106*, 27−34.

(411) Eren, T.; Kusefoglu, S. H. Synthesis and Polymerization of the Bromoacrylated Plant Oil Triglycerides to Rigid, Flame-Retardant Polymers. *J. Appl. Polym. Sci.* **2004**, *91*, 2700−2710.

(412) Chow, R. C. L.; Marvel, C. S. Copolymerization of Allyl Esters of Some Fatty Acids. *J. Polym. Sci. A: Polym. Chem.* **1968**, *6*, 1515−1521.

(413) Chang, S.-P.; Miwa, T. K. Allyl Esters of Crambe-Derived Long-Chain Fatty Acids and Their Polymers. *J. Appl. Polym. Sci.* **1979**, *24*, 441−454.

(414) Barbosa, J. V.; Veludo, E.; Moniz, J.; Magalhães, F. D.; Bastos, M. M. S. M. Synthesis and Characterization of Acrylic Fatty Acid Derivative and Use as Reactive Coalescing Agent. *Eur. J. Lipid Sci. Technol.* **2012**, *114*, 1175−1182.

(415) Maiti, B.; Kumar, S.; De, P. Controlled Raft Synthesis of Side-Chain Oleic Acid Containing Polymers and Their Post-Polymerization Functionalization. *RSC Adv.* **2014**, *4*, 56415−56423.

(416) Maiti, B.; De, P. Raft Polymerization of Fatty Acid Containing Monomers: Controlled Synthesis of Polymers from Renewable Resources. *RSC Adv.* **2013**, *3*, 24983−24990.

(417) Cho, H.-G.; Park, S.-Y.; Jegal, J.; Song, B.-K.; Kim, H.-J. Preparation and Characterization of Acrylic Polymers Based on a Novel Acrylic Monomer Produced from Vegetable Oil. *J. Appl. Polym. Sci.* **2009**, 736−742.

(418) Yuan, L.; Wang, Z.; Trenor, N. M.; Tang, C. Amidation of Triglycerides by Amino Alcohols and Their Impact on Plant Oil-Derived Polymers. *Polym. Chem.* **2016**, *7*, 2790−2798.

(419) Yuan, L.; Wang, Z.; Trenor, N. M.; Tang, C. Robust Amidation Transformation of Plant Oils into Fatty Derivatives for Sustainable Monomers and Polymers. *Macromolecules* **2015**, *48*, 1320−1328.

(420) Delatte, D.; Kaya, E.; Kolibal, L. G.; Mendon, S. K.; Rawlins, J. W.; Thames, S. F. Synthesis and Characterization of a Soybean Oil-Based Macromonomer. *J. Appl. Polym. Sci.* **2014**, *131*, 40249.

(421) Dey, T. Properties of Vinyl Ester Resins Containing Methacrylated Fatty Acid Comonomer: The Effect of Fatty Acid Chain Length. *Polym. Internat.* **2007**, *56*, 853−859.

(422) Can, E.; La Scala, J. J.; Sands, J. M.; Palmese, G. R. The Synthesis of 9-10 Dibromo Stearic Acid Glycidyl Methacrylate and Its Use in Vinyl Ester Resins. *J. Appl. Polym. Sci.* **2007**, *106*, 3833−3842.

(423) Li, S. H.; Yang, X. J.; Huang, K.; Li, M.; Xia, J. L. Preparation and Characterization of Dimer Fatty Acids-Based Vinyl Ester Resin Monomer. *Adv. Mater. Res.* **2013**, *721*, 86−89.

(424) Moreno, M.; Goikoetxea, M.; Barandiaran, M. J. Biobased-Waterborne Homopolymers from Oleic Acid Derivatives. *J. Polym. Sci. A: Polym. Chem.* **2012**, *50*, 4628−4637.

(425) Moreno, M.; Goikoetxea, M.; de la Cal, J. C.; Barandiaran, M. J. From Fatty Acid and Lactone Biobased Monomers toward Fully Renewable Polymer Latexes. *J. Polym. Sci. A: Polym. Chem.* **2014**, *52*, 3543−3549.

(426) La Scala, J. J.; Sands, J. M.; Orlicki, J. A.; Robinette, E. J.; Palmese, G. R. Fatty Acid-Based Monomers as Styrene Replacements for Liquid Molding Resins. *Polymer* **2004**, *45*, 7729−7737.

(427) Zych, A.; Tellers, J.; Bertolacci, L.; Ceseracciu, L.; Marini, L.; Mancini, G.; Athanassiou, A. Biobased, Biodegradable, Self-Healing Boronic Ester Vitrimers from Epoxidized Soybean Oil Acrylate. *ACS Appl. Polym. Mater.* **2021**, *3*, 1135−1144.

(428) Sainz, M. F.; Souto, J. A.; Regentova, D.; Johansson, M. K. G.; Timhagen, S. T.; Irvine, D. J.; Buijsen, P.; Koning, C. E.; Stockman, R. A.; Howdle, S. M. A Facile and Green Route to Terpene Derived Acrylate and Methacrylate Monomers and Simple Free Radical Polymerisation to Yield New Renewable Polymers and Coatings. *Polym. Chem.* **2016**, *7*, 2882−2887.

(429) Satoh, K. Controlled/Living Polymerization of Renewable Vinyl Monomers into Bio-Based Polymers. *Polym. J.* **2015**, *47*, 527−536.

(430) Nishida, T.; Satoh, K.; Kamigaito, M. Biobased Polymers Via Radical Homopolymerization and Copolymerization of a Series of Terpenoid-Derived Conjugated Dienes with Exo-Methylene and 6-Membered Ring. *Molecules* **2020**, *25*, 5890.

(431) Cravero, R. M.; Gonzalez-Sierra, M.; Labadie, G. R. Labadie, Convergent Approaches to Saudin Intermediates. *Helv. Chim. Acta* **2003**, *86*, 2741−2753.

(432) Zweifel, G.; Brown, H. C. Hydroboration of Terpenes. Ii. The Hydroboration of a- and /3-Pinene—the Absolute Configuration of the Dialkylborane from the Hydroboration of a-Pinene. *J. American Chem. Soc.* **1964**, *86*, 393−397.

(433) Elamparuthi, E.; Fellay, C.; Neuburger, M.; Gademann, K. Total Synthesis of Cyrneine A. *Angew. Chem., Int. Ed.* **2012**, *51*, 4071−3.

(434) Chen, M. S.; Prabagaran, N.; Labenz, N. A.; White, M. C. Christina White, Serial Ligand Catalysis: A Highly Selective Allylic C-H Oxidati. *J. American Chem. Soc.* **2005**, *127*, 6970−6971.

(435) Coumes, F.; Balarezo, M.; Rieger, J.; Stoffelbach, F. Biobased Amphiphilic Block Copolymers by Raft-Mediated Pisa in Green-solvent. *Macromol. Rap. Commun.* **2020**, *41*, 2000002.

(436) Liu, S.; Mishra, M. K. Atom Transfer Radical Polymerization of Menthyl Acrylate. *Macromolecules* **2007**, *40*, 867−871.

(437) Noppalit, S.; Simula, A.; Ballard, N.; Callies, X.; Asua, J. M.; Billon, L. Renewable Terpene Derivative as a Biosourced Elastomeric Building Block in the Design of Functional Acrylic Copolymers. *Biomacromolecules* **2019**, *20*, 2241−2251.

(438) Min, E. H.; Wong, K. H.; Setijadi, E.; Ladouceur, F.; Straton, M.; Argyros, A. Menthol-Based Chiral Copolymers for Polymer Optical Fibres (Pof). *Polym. Chem.* **2011**, *2*, 2045−2051.

(439) Baek, S.-S.; Hwang, S.-H. Preparation and Adhesion Performance of Transparent Acrylic Pressure-Sensitive Adhesives Containing Menthyl Acrylate. *Polym. Bull.* **2016**, *73*, 687−701.

(440) Droesbeke, M. A.; Simula, A.; Asua, J. M.; Du Prez, F. E. Biosourced Terpenoids for the Development of Sustainable Acrylic Pressure-Sensitive Adhesives Via Emulsion Polymerisation. *Green Chem.* **2020**, *22*, 4561−4569.

(441) Stamm, A.; Tengdelius, M.; Schmidt, B.; Engström, J.; Syrén, P. O.; Fogelström, L.; Malmström, E. Chemo-Enzymatic Pathways toward Pinene-Based Renewable Materials. *Green Chem.* **2019**, *21*, 2720−2731.

(442) Lima, M. S.; Costa, C. S. M. F.; Coelho, J. F. J.; Fonseca, A. C.; Serra, A. C. A Simple Strategy toward the Substitution of Styrene by Sobrerol-Based Monomers in Unsaturated Polyester Resins. *Green Chem.* **2018**, *20*, 4880−4890.

(443) Draczyńska, B. C. C.; Siewiński, Dr. A.; Rymkiewicz, A.; Zabźa, A.; Leufvèn, A. Biotransformation of Pinenes Xvii. Transformation of A-and B-Pinenes by Means of Armillariella Mellea (Honey Fungus), a Parasite of Woodlands. *J. Basic Microbiol.* **1985**, *25*, 487−492.

(444) Liu, W.; Xie, T.; Qiu, R. Biobased Thermosets Prepared from Rigid Isosorbide and Flexible Soybean Oil Derivatives. *ACS Sus. Chem. Eng.* **2017**, *5*, 774−783.

(445) Rose, M.; Palkovits, R. Isosorbide as a Renewable Platform Chemical for Versatile Applications-Quo Vadis? *ChemSusChem* **2012**, *5*, 167−76.

(446) Yu, D.; Zhao, J.; Wang, W.; Qi, J.; Hu, Y. Mono-Acrylated Isosorbide as a Bio-Based Monomer for the Improvement of Thermal and Mechanical Properties of Poly(Methyl Methacrylate). *RSC Adv.* **2019**, *9*, 35532−35538.

(447) Łukaszczyk, J.; Janicki, B.; Kaczmarek, M. Synthesis and Properties of Isosorbide Based Epoxy Resin. *Eur. Polym. J.* **2011**, *47*, 1601−1606.

(448) Dussenne, C.; Delaunay, T.; Wiatz, V.; Wyart, H.; Suisse, I.; Sauthier, M. Synthesis of Isosorbide: An Overview of Challenging Reactions. *Green Chem.* **2017**, *19*, 5332−5344.

(449) Zhang, X.; Durndell, L. J.; Isaacs, M. A.; Parlett, C. M. A.; Lee, A. F.; Wilson, K. Platinum-Catalyzed Aqueous-Phase Hydrogenation of D-Glucose to D-Sorbitol. *ACS Catal.* **2016**, *6*, 7409−7417.

(450) Romero, A.; Nieto-Márquez, A.; Alonso, E. Bimetallic Ru:Ni/Mcm-48 Catalysts for the Effective Hydrogenation of D -Glucose into Sorbitol. *Appl. Catal. A: General* **2017**, *529*, 49−59.

(451) Salzburg, H.; Meyborg, H.; Ziemann, H. Process for the Preparation of 1,4-3,6-Dianhydro-Hexitols. US 4408061A, 1983.

(452) Fleche, G.; Huchette, M. Isosorbide. Preparation, Properties and Chemistry. *Starch/Starke* **1986**, *38*, 26−30.

(453) Kobayashi, S.; Manabe, K. Development of Novel Lewis Acid Catalysts for Selective Organic Reactions in Aqueous Media. *Acc. Chem. Res.* **2002**, *35*, 209−217.

(454) Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W.-L. Lam, Rare-Earth Metal Triflates in Organic Synthesis. *Chem. Rev.* **2002**, *102*, 2227−2302.

(455) Liu, F.; De Oliveira Vigier, K.; Pera-Titus, M.; Pouilloux, Y.; Clacens, J.-M.; Decampo, F.; Jérôme, F. Catalytic Etherification of Glycerol with Short Chain Alkyl Alcohols in the Presence of Lewis Acids. *Green Chem.* **2013**, *15*, 901−909.

(456) Yamaguchi, A.; Muramatsu, N.; Mimura, N.; Shirai, M.; Sato, O. Intramolecular Dehydration of Biomass-Derived Sugar Alcohols in High-Temperature Water. *Phys. Chem. Chem. Phys.* **2017**, *19*, 2714−2722.

(457) Yamaguchi, A.; Hiyoshi, N.; Sato, O.; Shirai, M. Sorbitol Dehydration in High Temperature Liquid Water. *Green Chem.* **2011**, *13*, 873−881.

(458) Vilcocq, L.; Cabiac, A.; Especel, C.; Lacombe, S.; Duprez, D. Hydrocarbon Fuel Synthesis from Sorbitol over Bifunctional Catalysts: Association of Tungstated Titania with Platinum, Palladium or Iridium. *Catal. Today* **2015**, *242*, 91−100.

(459) Vilcocq, L.; Cabiac, A.; Especel, C.; Lacombe, S.; Duprez, D. Catherine Especel, Sylvie Lacombe, Daniel Duprez, New Insights into the Mechanism of Sorbitol Transformation over an Original Bifunctional Catalytic System. *J. Catal.* **2014**, *320*, 16−25.

(460) Rusu, O. A.; Hoelderich, W. F.; Wyart, H.; Ibert, M. Metal Phosphate Catalyzed Dehydration of Sorbitol under Hydrothermal Conditions. *Appl. Catal. B: Environ.* **2015**, *176-177*, 139−149.

(461) Otomo, R.; Yokoi, T.; Tatsumi, T. Synthesis of Isosorbide from Sorbitol in Water over High-Silica Aluminosilicate Zeolites. *Appl. Catal. A: General* **2015**, *505*, 28−35.

(462) Kobayashi, H.; Yokoyama, H.; Feng, B.; Fukuoka, A. Dehydration of Sorbitol to Isosorbide over H-Beta Zeolites with High Si/Al Ratios. *Green Chem.* **2015**, *17*, 2732−2735.

(463) Sun, P.; Yu, D. H.; Hu, Y.; Tang, Z. C.; Xia, J. J.; Li, H.; Huang, H. H3pw12o40/Sio2 for Sorbitol Dehydration to Isosorbide: High Efficient and Reusable Solid Acid Catalyst. *Korean J. Chem. Eng.* **2011**, *28*, 99−105.

(464) Barbaro, P.; Liguori, F.; Moreno-Marrodan, C. Selective Direct Conversion of C5 and C6 Sugars to High Added-Value Chemicals by a Bifunctional, Single Catalytic Body. *Green Chem.* **2016**, *18*, 2935−2940.

(465) de Almeida, R. M.; Li, J.; Nederlof, C.; O'Connor, P.; Makkee, M.; Moulijn, J. A. Cellulose Conversion to Isosorbide in Molten Salt Hydrate Media. *ChemSusChem* **2010**, *3*, 325−8.

(466) Mansoori, Y.; Hemmati, S.; Eghbali, P.; Zamanloo, M. R.; Imanzadeh, G. Nanocomposite Materials Based on Isosorbide Methacrylate/Cloisite 20a. *Polym. Internat.* **2013**, *62*, 280−288.

(467) Lub, J.; Vogels, J. P. A.; Wegh, R. T.; Nijssen, W. P. M. Isosorbide Derivatives. WO 03027119A1, 2003.

(468) Gallagher, J. J.; Hillmyer, M. A.; Reineke, T. M. Isosorbide-Based Polymethacrylates. *ACS Sus. Chem. Eng.* **2015**, *3*, 662−667.

(469) Gallagher, J. J.; Hillmyer, M. A.; Reineke, T. M. Acrylic Triblock Copolymers Incorporating Isosorbide for Pressure Sensitive Adhesives. *ACS Sus. Chem. Eng.* **2016**, *4*, 3379−3387.

(470) Baek, S.-S.; Jang, S.-H.; Hwang, S.-H. Sustainable Isosorbide-Based Transparent Pressure-Sensitive Adhesives for Optically Clear Adhesive and Their Adhesion Performance. *Polym. Internat.* **2017**, *66*, 1834−1840.

(471) Matt, L.; Parve, J.; Parve, O.; Pehk, T.; Pham, T. H.; Liblikas, I.; Vares, L.; Jannasch, P. Enzymatic Synthesis and Polymerization of Isosorbide-Based Monomethacrylates for High-Tg Plastics. *ACS Sus. Chem. Eng.* **2018**, *6*, 17382−17390.

(472) Badía, A.; Agirre, A.; Barandiaran, M. J.; Leiza, J. R. Easy Removable and Uv Tunable Biobased Waterborne Pressure Sensitive Adhesives. *Int. J. Adhes. Adhes.* **2021**, *108*, 102860.

(473) Howell, B. A.; Daniel, Y. G. Synthesis and Characterization of Isomeric Diphenylphosphatoisosorbide Acrylates. *Phosphorus Sulfur Silicon Relat. Elem.* **2020**, *195*, 638−643.

(474) Badia, A.; Agirre, A.; Barandiaran, M. J.; Leiza, J. R. Removable Biobased Waterborne Pressure-Sensitive Adhesives Containing Mixtures of Isosorbide Methacrylate Monomers. *Biomacromolecules* **2020**, *21*, 4522−4531.

(475) Sadler, J. M.; Nguyen, A.-P. T.; Toulan, F. R.; Szabo, J. P.; Palmese, G. R.; Scheck, C.; Lutgen, S.; La Scala, J. J. Isosorbide-Methacrylate as a Bio-Based Low Viscosity Resin for High

Performance Thermosetting Applications. *J. Mater. Chem. A* **2013**, *1*, 12579−12586.

(476) Mosnacek, J.; Matyjaszewski, K. Atom Transfer Radical Polymerization of Tulipalin A: A Naturally Renewable Monomer. *Macromolecules* **2008**, *41*, 5509−5511.

(477) van Rossum, M. W.P.C.; Alberda, M.; van der Plas, L. H.W. Tulipaline and Tuliposide in Cultured Explants of Tulip Bulb Scales. *Phytochem* **1998**, *49*, 723−729.

(478) Hoffmann, H. M. R.; Rabe, J. Synthesis and Biological Activity of a-Methylene-Y-Butyrolactones. *Angew. Chem., Int. Ed.* **1985**, *24*, 94−110.

(479) Zhang, Y.; Miyake, G. M.; Chen, E. Y. Alane-Based Classical and Frustrated Lewis Pairs in Polymer Synthesis: Rapid Polymerization of Mma and Naturally Renewable Methylene Butyrolactones into High-Molecular-Weight Polymers. *Angew. Chem., Int. Ed.* **2010**, *49*, 10158−62.

(480) Park, B. K.; Nakagawa, M.; Hirota, A.; Nakayama, M. Methylenolactocin, a Novel Antitumor Antibiotic from Penicillum Sp. *J. Antibiot.* **1988**, *41*, 751−758.

(481) Kitson, R. R.; Millemaggi, A.; Taylor, R. J. The Renaissance of Alpha-Methylene-Gamma-Butyrolactones: New Synthetic Approaches. *Angew. Chem., Int. Ed.* **2009**, *48*, 9426−51.

(482) Stansbury, J. W.; Antonucci, J. M. Evaluation of Methylene Lactone Monomers in Dental Resins. *Dent. Mater. J.* **1992**, *8*, 270−273.

(483) Mousa, M.; Bergenudd, H.; Kron, A. L.; Malmström, E. Biobased Lactones—Exploring Their Free-Radical Polymerization and Polymer Properties. *Macromolecules* **2021**, *54*, 6127−6134.

(484) Pérocheau Arnaud, S.; Andreou, E.; Pereira Köster, L. V. G.; Robert, T. Selective Synthesis of Monoesters of Itaconic Acid with Broad Substrate Scope: Biobased Alternatives to Acrylic Acid? *ACS Sus. Chem. Eng.* **2020**, *8*, 1583−1590.

(485) Trotta, J. T.; Jin, M.; Stawiasz, K. J.; Michaudel, Q.; Chen, W.-L.; Fors, B. P. Synthesis of Methylene Butyrolactone Polymers from Itaconic Acid. *J. Polym. Sci. A: Polym. Chem.* **2017**, *55*, 2730−2737.

(486) Gowda, R. R.; Chen, E. Y. X. Synthesis of Β-Methyl-Α-Methylene-Γ-Butyrolactone from Biorenewable Itaconic Acid. *Org. Chem. Front.* **2014**, *1*, 230−234.

(487) Murray, A. W.; Reid, R. G. Convenient Synthesis of a-Epoxylactones (4-Oxo-1,5-Dioxaspiro[2.4[Heptanes and -[2.5]-Octantes. *Synth.* **1985**, *1985*, 35−38.

(488) Bensabeh, N.; Moreno, A.; Roig, A.; Monaghan, O. R.; Ronda, J. C.; Cadiz, V.; Galia, M.; Howdle, S. M.; Lligadas, G.; Percec, V. Polyacrylates Derived from Biobased Ethyl Lactate Solvent Via Set-Lrp. *Biomacromolecules* **2019**, *20*, 2135−2147.

(489) Candy, M.; Tomas, L.; Parat, S.; Heran, V.; Bienayme, H.; Pons, J.-M.; Bressy, C. A Convergent Approach to (−)-Callystatin a Based on Local Symmetry. *Chem. Eur. J.* **2012**, *18*, 14267−14271.

(490) Baker, B. R.; Schaub, R. E.; Williams, J. H. An Antimalarial Alkaloid from Hydrangea. Xi. Synthesis of 3-[Β-Keto-Y-(3- and 4-Hydroxymethyl-2-Pyrrolidyl)Propyl]-4-Quinazolones. *J. Org. Chem.* **1952**, *17*, 116−131.

(491) Brieger, G.; Nestrick, T. J. Catalytic Transfer Hydrogenation. *Chem. Rev.* **1974**, *74*, 567−580.

(492) Paryzek, Z.; Koenig, H.; Tabaczka, B. Ammonium Formate/Palladium on Carbon: A Versatile System for Catalytic Hydrogen Transfer Reductions of Carbon-Carbon Double Bonds. *Synth.* **2003**, 2023−2026.

(493) Zhang, Y.; Chen, E. Y. Conjugate-Addition Organopolymerization: Rapid Production of Acrylic Bioplastics by N-Heterocyclic Carbenes. *Angew. Chem., Int. Ed.* **2012**, *51*, 2465−9.

(494) Zhang, Y.; Schmitt, M.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y. Organocatalytic Conjugate-Addition Polymerization of Linear and Cyclic Acrylic Monomers by N-Heterocyclic Carbenes: Mechanisms of Chain Initiation, Propagation, and Termination. *J. American Chem. Soc.* **2013**, *135*, 17925−42.

(495) Mosnáček, J.; Yoon, J. A.; Juhari, A.; Koynov, K.; Matyjaszewski, K. Synthesis, Morphology and Mechanical Properties of Linear Triblock Copolymers Based on Poly(Α-Methylene-Γ-Butyrolactone). *Polymer* **2009**, *50*, 2087−2094.

(496) Ray, P.; Hughes, T.; Smith, C.; Simon, G. P.; Saito, K. Synthesis of Bioacrylic Polymers from Dihydro-5-Hydroxyl Furan-2-One (2h-Hbo) by Free and Controlled Radical Polymerization. *ACS Omega* **2018**, *3*, 2040−2048.

(497) Camp, J. E. Bio-Available Solvent Cyrene: Synthesis, Derivatization, and Applications. *ChemSusChem* **2018**, *11*, 3048−3055.

(498) Peru, A. A.; Flourat, A. L.; Gunawan, C.; Raverty, W.; Jevric, M.; Greatrex, B. W.; Allais, F. Chemo-Enzymatic Synthesis of Chiral Epoxides Ethyl and Methyl (S)-3-(Oxiran-2-Yl)Propanoates from Renewable Levoglucosenone: An Access to Enantiopure (S)-Dairy Lactone. *Molecules* **2016**, *21*, 988.

(499) Comba, M. B.; Tsai, Y.-h.; Sarotti, A. M.; Mangione, M. I.; Suárez, A. G.; Spanevello, R. A. Levoglucosenone and Its New Applications: Valorization of Cellulose Residues. *Eur. J. Org. Chem.* **2018**, *2018*, 590−604.

(500) Shibagaki, M.; Takahashi, K.; Kuno, H.; Honda, I.; Matsushita, H. Ichiro Honda and Hajime Matsushita, Synthesis of Levoglucosenone. *Chem. Lett.* **1990**, *19*, 307−310.

(501) Meng, X.; Zhang, H.; Liu, C.; Xiao, R. Comparison of Acids and Sulfates for Producing Levoglucosan and Levoglucosenone by Selective Catalytic Fast Pyrolysis of Cellulose Using Py-Gc/Ms. *Energy Fuels* **2016**, *30*, 8369−8376.

(502) De bruyn, M.; Fan, J.; Budarin, V. L.; Macquarrie, D. J.; Gomez, L. D.; Simister, R.; Farmer, T. J.; Raverty, W. D.; McQueen-Mason, S. J.; Clark, J. H. A New Perspective in Bio-Refining: Levoglucosenone and Cleaner Lignin from Waste Biorefinery Hydrolysis Lignin by Selective Conversion of Residual Saccharides. *Energy & Environ. Sci.* **2016**, *9*, 2571−2574.

(503) Wilson, K. L.; Kennedy, A. R.; Murray, J.; Greatrex, B.; Jamieson, C.; Watson, A. J. Scope and Limitations of a Dmf Bio-Alternative within Sonogashira Cross-Coupling and Cacchi-Type Annulation. *Beilstein J. Org. Chem.* **2016**, *12*, 2005−2011.

(504) Sherwood, J.; De bruyn, M.; Constantinou, A.; Moity, L.; McElroy, C. R.; Farmer, T. J.; Duncan, T.; Raverty, W.; Hunt, A. J.; Clark, J. H. Dihydrolevoglucosenone (Cyrene) as a Bio-Based Alternative for Dipolar Aprotic Solvents. *Chem. Commun. (Cambridge)* **2014**, *50*, 9650−2.

(505) Koseki, K.; Ebata, T.; Kawakami, H.; Matsushita, H.; Naoi, Y.; Itoh, K. A Method for Easy Preparation of Optically Pure (S)-5-Hydroxy-2-Penten-4-Olide and (S)-5-Hydroxypentan-4-Olide. *Heterocycles* **1990**, *31*, 423−426.

(506) Zamzow, M.; Hocker, H. Synthesis of Polymers with Pendant Spiro Orthoester Groups. *Macromol. Chem. Phys.* **1994**, *195*, 2381−2400.

(507) Diot-Néant, F.; Rastoder, E.; Miller, S. A.; Allais, F. Chemo-Enzymatic Synthesis and Free Radical Polymerization of Renewable Acrylate Monomers from Cellulose-Based Lactones. *ACS Sus. Chem. Eng.* **2018**, *6*, 17284−17293.

(508) Ray, P.; Hughes, T.; Smith, C.; Hibbert, M.; Saito, K.; Simon, G. P. Development of Bio-Acrylic Polymers from Cyrene: Transforming a Green Solvent to a Green Polymer. *Polym. Chem.* **2019**, *10*, 3334−3341.

(509) Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S.; Cramail, H. From Lignin-Derived Aromatic Compounds to Novel Biobased Polymers. *Macromol. Rap. Commun.* **2016**, *37*, 9−28.

(510) Fache, M.; Boutevin, B.; Caillol, S. Epoxy Thermosets from Model Mixtures of the Lignin-to-Vanillin Process. *Green Chem.* **2016**, *18*, 712−725.

(511) Molina-Gutierrez, S.; Dalle Vacche, S.; Vitale, A.; Ladmiral, V.; Caillol, S.; Bongiovanni, R.; Lacroix-Desmazes, P. Photoinduced Polymerization of Eugenol-Derived Methacrylates. *Molecules* **2020**, *25*, 3444.

(512) Brazinha, C.; Barbosa, D. S.; Crespo, J. G. Sustainable Recovery of Pure Natural Vanillin from Fermentation Media in a Single Pervaporation Step. *Green Chem.* **2011**, *13*, 2197−2203.

(513) Fache, M.; Boutevin, B.; Caillol, S. Vanillin Production from Lignin and Its Use as a Renewable Chemical. *ACS Sus. Chem. Eng.* **2016**, *4*, 35−46.

(514) Brodin, I.; Sjöholm, E.; Gellerstedt, G. The Behavior of Kraft Lignin During Thermal Treatment. *J. Anal. Appl. Pyrolysis.* **2010**, *87*, 70−77.

(515) Yao, K.; Tang, C. Controlled Polymerization of Next-Generation Renewable Monomers and Beyond. *Macromolecules* **2013**, *46*, 1689−1712.

(516) Shen, X.; Meng, Q.; Mei, Q.; Liu, H.; Yan, J.; Song, J.; Tan, D.; Chen, B.; Zhang, Z.; Yang, G.; et al. Selective Catalytic Transformation of Lignin with Guaiacol as the Only Liquid Product. *Chem. Sci.* **2020**, *11*, 1347−1352.

(517) Stanzione, J. F., III; Sadler, J. M.; La Scala, J. J.; Reno, K. H.; Wool, R. P. Vanillin-Based Resin for Use in Composite Applications. *Green Chem.* **2012**, *14*, 2346−2352.

(518) Holmberg, A. L.; Stanzione, J. F.; Wool, R. P.; Epps, T. H. A Facile Method for Generating Designer Block Copolymers from Functionalized Lignin Model Compounds. *ACS Sus. Chem. Eng.* **2014**, *2*, 569−573.

(519) Holmberg, A. L.; Karavolias, M. G.; Epps, T. H. Raft Polymerization and Associated Reactivity Ratios of Methacrylate-Functionalized Mixed Bio-Oil Constituents. *Polym. Chem.* **2015**, *6*, 5728−5739.

(520) Holmberg, A. L.; Nguyen, N. A.; Karavolias, M. G.; Reno, K. H.; Wool, R. P.; Epps, T. H. Softwood Lignin-Based Methacrylate Polymers with Tunable Thermal and Viscoelastic Properties. *Macromolecules* **2016**, *49*, 1286−1295.

(521) Stanzione, J. F., 3rd; Sadler, J. M.; La Scala, J. J.; Wool, R. P. Lignin Model Compounds as Bio-Based Reactive Diluents for Liquid Molding Resins. *ChemSusChem* **2012**, *5*, 1291−7.

(522) Holmberg, A. L.; Reno, K. H.; Nguyen, N. A.; Wool, R. P.; Epps, T. H., 3rd Syringyl Methacrylate, a Hardwood Lignin-Based Monomer for High-Tg Polymeric Materials. *ACS Macro Lett.* **2016**, *5*, 574−578.

(523) Zhang, C.; Madbouly, S. A.; Kessler, M. R. Renewable Polymers Prepared from Vanillin and Its Derivatives. *Macromol. Chem. Phys.* **2015**, *216*, 1816−1822.

(524) Vergara, J. H.; Yadav, S. K.; Bolarin, O.; La Scala, J. J.; Palmese, G. R. Synthesis and Characterization of Low-Viscosity Bio-Based Styrene Alternatives for Bisphenol a Vinyl Ester Thermosetting Resins. *ACS Sus. Chem. Eng.* **2020**, *8*, 17234−17244.

(525) Abdelaty, M. S. A.; Kuckling, D. Poly (N-Isopropyl Acrylamide-Co-Vanillin Acrylate) Dual Responsive Functional Copolymers for Grafting Biomolecules by Schiff's Base Click Reaction. *Open J. Org. Polym. Mater.* **2018**, *08*, 15−32.

(526) Zhou, J.; Zhang, H.; Deng, J.; Wu, Y. High Glass-Transition Temperature Acrylate Polymers Derived from Biomasses, Syringaldehyde, and Vanillin. *Macromol. Chem. Phys.* **2016**, *217*, 2402−2408.

(527) Wang, S.; Shuai, L.; Saha, B.; Vlachos, D. G.; Epps, T. H., 3rd From Tree to Tape: Direct Synthesis of Pressure Sensitive Adhesives from Depolymerized Raw Lignocellulosic Biomass. *ACS Cent. Sci.* **2018**, *4*, 701−708.

(528) Badía, A.; Santos, J. I.; Agirre, A.; Barandiaran, M. J.; Leiza, J. R. Uv-Tunable Biobased Pressure-Sensitive Adhesives Containing Piperonyl Methacrylate. *ACS Sus. Chem. Eng.* **2019**, *7*, 19122−19130.

(529) Hu, Y.; Shang, Q.; Tang, J.; Wang, C.; Zhang, F.; Jia, P.; Feng, G.; Wu, Q.; Liu, C.; Hu, L.; et al. Use of Cardanol-Based Acrylate as Reactive Diluent in Uv-Curable Castor Oil-Based Polyurethane Acrylate Resins. *Ind. Crops Prod.* **2018**, *117*, 295−302.

(530) Ladmiral, V.; Jeannin, R.; Fernandes Lizarazu, K.; Lai-Kee-Him, J.; Bron, P.; Lacroix-Desmazes, P.; Caillol, S. Aromatic Biobased Polymer Latex from Cardanol. *Eur. Polym. J.* **2017**, *93*, 785−794.

(531) Ritter, J. J.; Minieri, P. P. A New Reaction of Nitriles. I. Amides from Alkenes and Mononitriles1. *J. American Chem. Soc.* **1948**, *70*, 4045−4048.

(532) Roe, E. T.; Swern, D. Fatty Acid Amides. Vi.2 Preparation of Substituted Amidostearic Acids by Addition of Nitriles to Oleic Acid3. *J. American Chem. Soc.* **1953**, *75*, 5479−5481.

(533) Blum, S.; Gertler, S.; Sarel, S.; Sinnreich, D. Formation and Mass Spectral Fragmentation of Ritter Products from Some Monoenic Fatty Acids. Location of Double-Bond Position in Unsaturated Acids. *J. Org. Chem.* **1972**, *37*, 3114−3120.

(534) Eren, T.; Kusefoglu, S. H. Synthesis and Polymerization of the Acrylamide Derivatives of Fatty Compounds. *J. Appl. Polym. Sci.* **2005**, *97*, 2264−2272.

(535) Tarnavchyk, I.; Popadyuk, A.; Popadyuk, N.; Voronov, A. Synthesis and Free Radical Copolymerization of a Vinyl Monomer from Soybean Oil. *ACS Sus. Chem. Eng.* **2015**, *3*, 1618−1622.

(536) Kohut, A.; Voronov, S.; Demchuk, Z.; Kirianchuk, V.; Kingsley, K.; Shevchuk, O.; Caillol, S.; Voronov, A. Non-Conventional Features of Plant Oil-Based Acrylic Monomers in Emulsion Polymerization. *Molecules* **2020**, *25*, 2990.

(537) Demchuk, Z.; Shevchuk, O.; Tarnavchyk, I.; Kirianchuk, V.; Kohut, A.; Voronov, S.; Voronov, A. Free Radical Polymerization Behavior of the Vinyl Monomers from Plant Oil Triglycerides. *ACS Sus. Chem. Eng.* **2016**, *4*, 6974−6980.

(538) Liu, H.; Lepoittevin, B.; Roddier, C.; Guerineau, V.; Bech, L.; Herry, J.-M.; Bellon-Fontaine, M.-N.; Roger, P. Facile Synthesis and Promising Antibacterial Properties of a New Guaiacol-Based Polymer. *Polymer* **2011**, *52*, 1908−1916.

(539) Song, Q.; Pascouau, C.; Zhao, J.; Zhang, G.; Peruch, F.; Carlotti, S. Ring-Opening Polymerization of Γ-Lactones and Copolymerization with Other Cyclic Monomers. *Prog. Polym. Sci.* **2020**, *110*, 101309−101309.

(540) Woodruff, M. A.; Hutmacher, D. W. The Return of a Forgotten Polymer—Polycaprolactone in the 21st Century. *Prog. Polym. Sci.* **2010**, *35*, 1217−1256.

(541) Zhang, X. Y.; Yang, H. L.; Yang, G. X.; Li, S. W.; Wang, X.; Ma, J. T. Metal-Free Mesoporous Sio2 Nanorods as a Highly Efficient Catalyst for the Baeyer-Villiger Oxidation under Mild Conditions. *ACS Sus. Chem. Eng.* **2018**, *6*, 5868−5876.

(542) Zhang, Y.; Zhao, Y.; Jiang, W.; Yao, Q.; Li, Z.; Gao, X.; Liu, T.; Yang, F.; Wang, F.; Liu, J. Lipase-Catalyzed Oxidation of Cyclohexanone to Form E-Caprolactone and Kinetic Modeling. *ACS Sus. Chem. Eng.* **2019**, *7*, 13294−13306.

(543) Champagne, E.; Strandman, S.; Zhu, X. X. Recent Developments and Optimization of Lipase-Catalyzed Lactone Formation and Ring-Opening Polymerization. *Macromol. Rap. Commun.* **2016**, *37*, 1986−2004.

(544) Tu, C.; Chen, J.; Li, W.; Wang, H.; Deng, K.; Vinokurov, V. A.; Huang, W. Hydrodeoxygenation of Bio-Derived Anisole to Cyclohexane over Bi-Functional Im-5 Zeolite Supported Ni Catalysts. *Sus. Energy & Fuels* **2019**, *3*, 3462−3472.

(545) Pennec, A.; Hollmann, F.; Smit, M. S.; Opperman, D. J. One-Pot Conversion of Cycloalkanes to Lactones. *ChemCatChem.* **2015**, *7*, 236−239.

(546) Schafer, L.; Buhler, K.; Karande, R.; Buhler, B. Rational Engineering of a Multi-Step Biocatalytic Cascade for the Conversion of Cyclohexane to Polycaprolactone Monomers Inpseudomonas Taiwanensis. *Biotechnol. J.* **2020**, *15*, 2000091.

(547) Beardslee, T.; Picataggio, S. Bio-Based Adipic Acid from Renewable Oils. *Lipid Technol.* **2012**, *24*, 223−225.

(548) Pyo, S.-H.; Park, J. H.; Srebny, V.; Hatti-Kaul, R. A Sustainable Synthetic Route for Biobased 6-Hydroxyhexanoic Acid, Adipic Acid and E-Caprolactone by Integrating Bio- and Chemical Catalysis. *Green Chem.* **2020**, *22*, 4450−4455.

(549) Buntara, T.; Noel, S.; Phua, P. H.; Melián-Cabrera, I.; De Vries, J. G.; Heeres, H. J. Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone. *Angew. Chem., Int. Ed.* **2011**, *50*, 7083−7087.

(550) Jiang, J.-W.; Tu, C.-C.; Chen, C.-H.; Lin, Y.-C. Highly Selective Silica-Supported Copper Catalysts Derived from Copper Phyllosilicates in the Hydrogenation of Adipic Acid to 1,6-Hexanediol. *ChemCatChem.* **2018**, *10*, 5449−5458.

(551) Touchy, A. S.; Shimizu, K.-i. Acceptorless Dehydrogenative Lactonization of Diols by Pt-Loaded Sno2 Catalysts. *RSC Adv.* **2015**, *5*, 29072−29075.

(552) Khamespanah, F.; Marx, M.; Crochet, D. B.; Pokharel, U. R.; Fronczek, F. R.; Maverick, A. W.; Beller, M. Oxalate Production Via Oxidation of Ascorbate Rather Than Reduction of Carbon Dioxide. *Nat. Commun.* **2021**, *12*, 1997.

(553) Pastero, L.; Curetti, N.; Ortenzi, M. A.; Schiavoni, M.; Destefanis, E.; Pavese, A. Co2 Capture and Sequestration in Stable Ca-Oxalate, Via Ca-Ascorbate Promoted Green Reaction. *Sci. Tot. Environ.* **2019**, *666*, 1232−1244.

(554) Quilter, H. C.; Hutchby, M.; Davidson, M. G.; Jones, M. D. Polymerisation of a Terpene-Derived Lactone: A Bio-Based Alternative to E-Caprolactone. *Polym. Chem.* **2017**, *8*, 833−837.

(555) Houk, K. N.; Jabbari, A.; Hall, H. K.; Aleman, C. Why Delta-Valerolactone Polymerizes and Gamma-Butyrolactone Does Not. *J. Org. Chem.* **2008**, *73*, 2674−2678.

(556) Asano, T.; Takagi, H.; Nakagawa, Y.; Tamura, M.; Tomishige, K. Selective Hydrogenolysis of 2-Furancarboxylic Acid to 5-Hydroxyvaleric Acid Derivatives over Supported Platinum Catalysts. *Green Chem.* **2019**, *21*, 6133−6145.

(557) Huang, K.; Brentzel, Z. J.; Barnett, K. J.; Dumesic, J. A.; Huber, G. W.; Maravelias, C. T. Conversion of Furfural to 1,5-Pentanediol: Process Synthesis and Analysis. *ACS Sus. Chem. Eng.* **2017**, *5*, 4699−4706.

(558) Wang, H. X.; Ding, G. Q.; Li, X. Q.; She, H. H.; Zhu, Y. L.; Li, Y. W. Sustainable Production of Gamma-Valerolactone and Delta-Valerolactone through the Coupling of Hydrogenation and Dehydrogenation. *Sus. Energy & Fuels* **2021**, *5*, 930−934.

(559) Hayes, G. C.; Becer, C. R. Levulinic Acid: A Sustainable Platform Chemical for Novel Polymer Architectures. *Polym. Chem.* **2020**, *11*, 4068−4077.

(560) Xu, S.; Wang, Y.; Hoye, T. R. Poly(4-Ketovalerolactone) from Levulinic Acid: Synthesis and Hydrolytic Degradation. *Macromolecules* **2020**, *53*, 4952−4959.

(561) Zhang, C. Q.; Schneiderman, D. K.; Cai, T.; Tai, Y. S.; Fox, K.; Zhang, K. C. Optically Active Beta-Methyl-Delta-Valerolactone: Biosynthesis and Polymerization. *ACS Sus. Chem. Eng.* **2016**, *4*, 4396−4402.

(562) Hong, M.; Chen, E. Y. X. Completely Recyclable Biopolymers with Linear and Cyclic Topologies Via Ring-Opening Polymerization of Γ-Butyrolactone. *Nat. Chem.* **2016**, *8*, 42−49.

(563) Hong, M.; Chen, E. Y. X. Towards Truly Sustainable Polymers: A Metal-Free Recyclable Polyester from Biorenewable Non-Strained -Butyrolactone. *Angew. Chem., Int. Ed.* **2016**, *55*, 4188−4193.

(564) Gallezot, P. Conversion of Biomass to Selected Chemical Products. *Chem. Soc. Rev.* **2012**, *41*, 1538−1558.

(565) Heisig, C.; Diedenhoven, J.; Jensen, C.; Gehrke, H.; Turek, T. Selective Hydrogenation of Biomass-Derived Succinic Acid: Reaction Network and Kinetics. *Chem. Eng. Technol.* **2020**, *43*, 484−492.

(566) Figueredo, A. L.; Costa, C. S.; Gothe, M. L.; Rossi, L. M.; Bazito, R. C.; Vidinha, P.; Pereira, C. G. Process Optimization for a Sustainable and Selective Conversion of Fumaric Acid into Γ-Butyrolactone over Pd-Re/Sio2. *Catal. Lett.* **2021**, *151*, 1821−1833.

(567) Hong, U. G.; Hwang, S.; Seo, J. G.; Yi, J.; Song, I. K. Hydrogenation of Succinic Acid to Γ-Butyrolactone over Palladium Catalyst Supported on Mesoporous Alumina Xerogel. *Catal. Lett.* **2010**, *138*, 28−33.

(568) Hong, U. G.; Lee, J.; Hwang, S.; Song, I. K. Hydrogenation of Succinic Acid to Γ-Butyrolactone (Gbl) over Palladium-Alumina Composite Catalyst Prepared by a Single-Step Sol-Gel Method. *Catal. Lett.* **2011**, *141*, 332−338.

(569) Hong, U. G.; Hwang, S.; Seo, J. G.; Lee, J.; Song, I. K. Hydrogenation of Succinic Acid to Γ-Butyrolactone (Gbl) over Palladium Catalyst Supported on Alumina Xerogel: Effect of Acid Density of the Catalyst. *J. Ind. Eng. Chem.* **2011**, *17*, 316−320.

(570) Zhang, C.; Chen, L.; Cheng, H.; Zhu, X.; Qi, Z. Atomically Dispersed Pd Catalysts for the Selective Hydrogenation of Succinic Acid to Γ-Butyrolactone. *Catal. Today* **2016**, *276*, 55−61.

(571) Chung, S.-H.; Park, Y.-M.; Kim, M.-S.; Lee, K.-Y. The Effect of Textural Properties on the Hydrogenation of Succinic Acid Using Palladium Incorporated Mesoporous Supports. *Catal. Today* **2012**, *185*, 205−210.

(572) Ly, B. K.; Minh, D. P.; Pinel, C.; Besson, M.; Tapin, B.; Epron, F.; Especel, C. Effect of Addition Mode of Re in Bimetallic Pd-Re/Tio2 Catalysts Upon the Selective Aqueous-Phase Hydrogenation of Succinic Acid to 1,4-Butanediol. *Top. Catal.* **2012**, *55*, 466−473.

(573) Ly, B. K.; Tapin, B.; Aouine, M.; Delichere, P.; Epron, F.; Pinel, C.; Especel, C.; Besson, M. Insights into the Oxidation State and Location of Rhenium in Re-Pd/Tio2 Catalysts for Aqueous-Phase Selective Hydrogenation of Succinic Acid to 1,4-Butanediol as a Function of Palladium and Rhenium Deposition Methods. *ChemCatChem.* **2015**, *7*, 2161−2178.

(574) Takeda, Y.; Tamura, M.; Nakagawa, Y.; Okumura, K.; Tomishige, K. Hydrogenation of Dicarboxylic Acids to Diols over Re-Pd Catalysts. *Catal. Sci. Technol.* **2016**, *6*, 5668−5683.

(575) Shao, Z.; Li, C.; Di, X.; Xiao, Z.; Liang, C. Aqueous-Phase Hydrogenation of Succinic Acid to Γ-Butyrolactone and Tetrahydrofuran over Pd/C, Re/C, and Pd-Re/C Catalysts. *Ind. Eng. Chem. Res.* **2014**, *53*, 9638−9645.

(576) Patankar, S. C.; Sharma, A. G.; Yadav, G. D. Biobased Process Intensification in Selective Synthesis of Gamma-Butyrolactone from Succinic Acid Via Synergistic Palladium-Copper Bimetallic Catalyst Supported on Alumina Xerogel. *Clean Technol. Environ. Policy* **2018**, *20*, 683−693.

(577) Rosi, L.; Frediani, M.; Frediani, P. Isotopomeric Diols by "One-Pot" Ru-Catalyzed Homogeneous Hydrogenation of Dicarboxylic Acids. *J. Organometal. Chem.* **2010**, *695*, 1314−1322.

(578) Chung, S. H.; Eom, H. J.; Kim, M. S.; Lee, M. S.; Lee, K. Y. Highly Dispersed Ruthenium Nanoparticle-Embedded Mesoporous Silica as a Catalyst for the Production of Gamma-Butyrolactone from Succinic Anhydride. *J. Nanosci. Nanotechnol* **2013**, *13*, 7701−7706.

(579) Hong, U. G.; Park, H. W.; Lee, J.; Hwang, S.; Song, I. K. Hydrogenation of Succinic Acid to Γ-Butyrolactone (Gbl) over Ruthenium Catalyst Supported on Surfactant-Templated Mesoporous Carbon. *J. Ind. Eng. Chem.* **2012**, *18*, 462−468.

(580) Kang, K. H.; Hong, U. G.; Bang, Y.; Choi, J. H.; Kim, J. K.; Lee, J. K.; Han, S. J.; Song, I. K. Hydrogenation of Succinic Acid to 1,4-Butanediol over Re-Ru Bimetallic Catalysts Supported on Mesoporous Carbon. *Appl. Catal. A: General* **2015**, *490*, 153−162.

(581) Hong, U. G.; Kim, J. K.; Lee, J.; Lee, J. K.; Song, J. H.; Yi, J.; Song, I. K. Hydrogenation of Succinic Acid to Tetrahydrofuran over Ruthenium-Carbon Composite Catalysts: Effect of Hcl Concentration in the Preparation of the Catalysts. *J. Ind. Eng. Chem.* **2014**, *20*, 3834−3840.

(582) Kang, K. H.; Hong, U. G.; Jun, J. O.; Song, J. H.; Bang, Y.; Choi, J. H.; Han, S. J.; Song, I. K. Hydrogenation of Succinic Acid to Γ-Butyrolactone and 1,4-Butanediol over Mesoporous Rhenium-Copper-Carbon Composite Catalyst. *J. Mol. Catal. A: Chem.* **2014**, *395*, 234−242.

(583) Kang, K. H.; Han, S. J.; Lee, J. W.; Kim, T. H.; Song, I. K. Effect of Boron Content on 1,4-Butanediol Production by Hydrogenation of Succinic Acid over Re-Ru/Bmc (Boron-Modified Mesoporous Carbon) Catalysts. *Appl. Catal. A: General* **2016**, *524*, 206−213.

(584) Di, X.; Shao, Z.; Li, C.; Li, W.; Liang, C. Hydrogenation of Succinic Acid over Supported Rhenium Catalysts Prepared by the Microwave-Assisted Thermolytic Method. *Catal. Sci. Technol.* **2015**, *5*, 2441−2448.

(585) Hong, U. G.; Park, H. W.; Lee, J.; Hwang, S.; Yi, J.; Song, I. K. Hydrogenation of Succinic Acid to Tetrahydrofuran (Thf) over Rhenium Catalyst Supported on H2so4-Treated Mesoporous Carbon. *Appl. Catal. A: General* **2012**, *415-416*, 141−148.

(586) Hamdan, M. A.; Lilic, A.; Vecino-Mantilla, M.; Nikitine, C.; Vilcocq, L.; Jahjah, M.; Pinel, C.; Perret, N. Influence of Reduction-Carburization Parameters on the Performance of Supported Molybdenum Carbide Catalysts in Succinic Acid Hydrogenation. *Ind. Eng. Chem. Res.* **2020**, *59*, 12964−12976.

(587) Keels, J. M.; Chen, X.; Karakalos, S.; Liang, C.; Monnier, J. R.; Regalbuto, J. R. Aqueous-Phase Hydrogenation of Succinic Acid

Using Bimetallic Ir-Re/C Catalysts Prepared by Strong Electrostatic Adsorption. *ACS Catal.* **2018**, *8*, 6486−6494.

(588) Lange, J.-P.; van der Heide, E.; van Buijtenen, J.; Price, R. Furfural—a Promising Platform for Lignocellulosic Biofuels. *ChemSusChem* **2012**, *5*, 150−166.

(589) Lan, J.; Chen, Z.; Lin, J.; Yin, G. Catalytic Aerobic Oxidation of Renewable Furfural to Maleic Anhydride and Furanone Derivatives with Their Mechanistic Studies. *Green Chem.* **2014**, *16*, 4351−4358.

(590) Choudhary, H.; Nishimura, S.; Ebitani, K. Metal-Free Oxidative Synthesis of Succinic Acid from Biomass-Derived Furan Compounds Using a Solid Acid Catalyst with Hydrogen Peroxide. *Appl. Catal. A: General* **2013**, *458*, 55−62.

(591) Zhu, R.; Zhou, G. Y.; Teng, J. N.; Liang, W. Y.; Li, X. L.; Fu, Y. Metal-Free Photocatalytic Aerobic Oxidation of Biomass-Based Furfural Derivatives to Prepare Gamma-Butyrolactone. *Green Chem.* **2021**, *23*, 1758−1765.

(592) Li, X. D.; Lan, X. C.; Wang, T. F. Highly Selective Catalytic Conversion of Furfural to Gamma-Butyrolactone. *Green Chem.* **2016**, *18*, 638−642.

(593) Li, X. D.; Wan, W. M.; Chen, J. G. G.; Wang, T. F. Selective Hydrogenation of Biomass-Derived 2(5h)-Furanone to Gamma-Butyrolactone over Ni-Based Bimetallic Catalysts. *ACS Sus. Chem. Eng.* **2018**, *6*, 16039−16046.

(594) Li, X. D.; Wan, W. M.; Kattel, S.; Chen, J. G. G.; Wang, T. F. Selective Hydrogenation of Biomass-Derived 2(5h)-Furanone over Pt-Ni and Pt-Co Bimetallic Catalysts: From Model Surfaces to Supported Catalysts. *J. Catal.* **2016**, *344*, 148−156.

(595) Li, X. D.; Li, Y. F.; Wang, T. F. Effect of Oxide Supports on Pt-Ni Bimetallic Catalysts for the Selective Hydrogenation of Biomass-Derived 2(5h)-Furanone. *Catal. Today* **2019**, *319*, 93−99.

(596) Chen, B. F.; Li, F. B.; Yuan, G. Q. Selective Hydrodeoxygenation of 5-Hydroxy-2(5h)-Furanone to Gamma-Butyrolactone over Pt/Mesoporous Solid Acid Bifunctional Catalyst. *RSC Adv.* **2017**, *7*, 21145−21152.

(597) Burgard, A.; Burk, M. J.; Osterhout, R.; Van Dien, S.; Yim, H. Development of a Commercial Scale Process for Production of 1,4-Butanediol from Sugar. *Curr. Opin. Biotechnol.* **2016**, *42*, 118−125.

(598) Kannapu, H. P. R.; Suh, Y.-W.; Narani, A.; Burri, D. R.; Kamaraju Seetha, R. R. Coupling of 1,4-Butanediol Dehydrogenation with Nitrobenzene Hydrogenation for Simultaneous Synthesis of Γ-Butyrolactone and Aniline over Promoted Cu-Mgo Catalysts: Effect of Promoters. *Catal. Lett.* **2017**, *147*, 90−101.

(599) Reddy, K. H. P.; Anand, N.; Venkateswarlu, V.; Rao, K. S. R.; Burri, D. R. A Selective Synthesis of 1-Phenylethanol and Γ-Butyrolactone through Coupling Processes over Cu/Mgo Catalysts. *J. Mol. Catal. A: Chem.* **2012**, *355*, 180−185.

(600) Onoda, M.; Nagano, Y.; Fujita, K.-i. Iridium-Catalyzed Dehydrogenative Lactonization of 1,4-Butanediol and Reversal Hydrogenation: New Hydrogen Storage System Using Cheap Organic Resources. *Int. J. Hydrog. Energy* **2019**, *44*, 28514−28520.

(601) Hwang, D. W.; Kashinathan, P.; Lee, J. M.; Lee, J. H.; Lee, U. h.; Hwang, J.-S.; Hwang, Y. K.; Chang, J.-S. Production of Γ-Butyrolactone from Biomass-Derived 1,4-Butanediol over Novel Copper-Silica Nanocomposite. *Green Chem.* **2011**, *13*, 1672−1675.

(602) Zhang, B.; Zhu, Y.; Ding, G.; Zheng, H.; Li, Y. Modification of the Supported Cu/Sio2 Catalyst by Alkaline Earth Metals in the Selective Conversion of 1,4-Butanediol to Γ-Butyrolactone. *Appl. Catal. A: General* **2012**, *443-444*, 191−201.

(603) Aellig, C.; Jenny, F.; Scholz, D.; Wolf, P.; Giovinazzo, I.; Kollhoff, F.; Hermans, I. Combined 1,4-Butanediol Lactonization and Transfer Hydrogenation/ Hydrogenolysis of Furfural-Derivatives under Continuous Flow Conditions. *Catal. Sci. Technol.* **2014**, *4*, 2326−2331.

(604) Nagaiah, P.; Venkat Rao, M.; Thirupathaiah, K.; Venkateshwarlu, V.; David Raju, B.; Rama Rao, K. S. Selective Vapour Phase Dehydrogenation of Biomass-Derived 1,4-Butanediol to Gamma Butyrolactone over Cu/Zro2 Catalysts: Influence of La2o3 Promotor. *Res. Chem. Intermed.* **2018**, *44*, 5817−5831.

(605) Bhanushali, J. T.; Prasad, D.; Patil, K. N.; Babu, G. V. R.; Kainthla, I.; Rao, K. S. R.; Jadhav, A. H.; Nagaraja, B. M. The Selectively Regulated Vapour Phase Dehydrogenation of 1,4-Butanediol to Gamma-Butyrolactone Employing a Copper-Based Ceria Catalyst. *New J. Chem.* **2019**, *43*, 11968−11983.

(606) Raju, M. A.; Gidyonu, P.; Nagaiah, P.; Rao, M. V.; Raju, B. D.; Rao, K. S. R. Mesoporous Silica-Supported Copper Catalysts for Dehydrogenation of Biomass-Derived 1,4-Butanediol to Gamma Butyrolactone in a Continuous Process at Atmospheric Pressure. *Biomass Convers. Biorefinery* **2019**, *9*, 719−726.

(607) Bhanushali, J. T.; Prasad, D.; Patil, K. N.; Reddy, K. S.; Kainthla, I.; Rao, K. S. R.; Jadhav, A. H.; Nagaraja, B. M. Tailoring the Catalytic Activity of Basic Mesoporous Cu/Ceo2 Catalyst by Al2o3 for Selective Lactonization and Dehydrogenation of 1,4-Butanediol to Γ-Butyrolactone. *Catal. Commun.* **2020**, *143*, 106049.

(608) Liu, H.; Jiang, Y.; Zhao, H.; Hou, Z. Preparation of Highly Dispersed Cu Catalysts from Hydrotalcite Precursor for the Dehydrogenation of 1,4-Butanediol. *J. Ind. Eng. Chem.* **2021**, *102*, 251−259.

(609) Huang, J.; Dai, W.-L.; Fan, K. Remarkable Support Crystal Phase Effect in Au/Feox Catalyzed Oxidation of 1,4-Butanediol to Γ-Butyrolactone. *J. Catal.* **2009**, *266*, 228−235.

(610) Zheng, J.; Huang, J.; Li, X.; Dai, W.-L.; Fan, K. Novel Magnetic-Separable and Efficient Au/Fe-Al-O Composite for the Lactonization of 1,4-Butanediol to Γ-Butyrolactone. *RSC Adv.* **2012**, *2*, 3801−3809.

(611) Li, X.; Cui, Y.; Yang, X.; Dai, W.-L.; Fan, K. Highly Efficient and Stable Au/Mn2o3 Catalyst for Oxidative Cyclization of 1,4-Butanediol to Γ-Butyrolactone. *Appl. Catal. A: General* **2013**, *458*, 63−70.

(612) Reddy, K. H. P.; Anand, N.; Prasad, P. S. S.; Rao, K. S. R.; Raju, B. D. Influence of Method of Preparation of Co-Cu/Mgo Catalyst on Dehydrogenation/Dehydration Reaction Pathway of 1, 4-Butanediol. *Catal. Commun.* **2011**, *12*, 866−869.

(613) Pillai, U. R.; Sahle-Demessie, E. Selective Hydrogenation of Maleic Anhydride to Γ-Butyrolactone over Pd/Al2o3 Catalyst Using Supercritical Co2 as Solvent. *Chem. Commun.* **2002**, 422−423.

(614) Pillai, U. R.; Sahle-Demessie, E.; Young, D. Maleic Anhydride Hydrogenation over Pd/Al2o3 Catalyst under Supercritical Co2Medium. *Appl. Catal. B: Environ.* **2003**, *43*, 131−138.

(615) Wang, Q.; Cheng, H.; Liu, R.; Hao, J.; Yu, Y.; Zhao, F. Influence of Metal Particle Size on the Hydrogenation of Maleic Anhydride over Pd/C Catalysts in Scco2. *Catal. Today* **2009**, *148*, 368−372.

(616) Yu, Y.; Guo, Y.; Zhan, W.; Guo, Y.; Wang, Y.; Wang, Y.; Zhang, Z.; Lu, G. Gas-Phase Hydrogenation of Maleic Anhydride to Γ-Butyrolactone at Atmospheric Pressure over Cu-Ceo2-Al2o3 Catalyst. *J. Mol. Catal. A: Chem.* **2011**, *337*, 77−81.

(617) Yu, Y.; Zhan, W.; Guo, Y.; Lu, G.; Adjimi, S.; Guo, Y. Gas-Phase Hydrogenation of Maleic Anhydride to Γ-Butyrolactone over Cu-Ceo2-Al2o3 Catalyst at Atmospheric Pressure: Effects of the Residual Sodium and Water in the Catalyst Precursor. *J. Mol. Catal. A: Chem.* **2014**, *395*, 392−397.

(618) Yu, Y.; Guo, Y. L.; Zhan, W. C.; Guo, Y.; Wang, Y. S.; Lu, G. Z. Effect of Promoters on Cu-Zno-Sio2 Catalyst for Gas-Phase Hydrogenation of Maleic Anhydride to Gamma-Butyrolactone at Atmospheric Pressure. *J. Mol. Catal. A: Chem.* **2014**, *392*, 1−7.

(619) Bertone, M. E.; Regenhardt, S. A.; Meyer, C. I.; Sebastian, V.; Garetto, T. F.; Marchi, A. J. Highly Selective Cu-Modified Ni/Sio2-Al2o3 Catalysts for the Conversion of Maleic Anhydride to Gamma-Butyrolactone in Gas Phase. *Top. Catal.* **2016**, *59*, 159−167.

(620) Bertone, M. E.; Meyer, C. I.; Regenhardt, S. A.; Sebastian, V.; Garetto, T. F.; Marchi, A. J. Highly Selective Conversion of Maleic Anhydride to Γ-Butyrolactone over Ni-Supported Catalysts Prepared by Precipitation-Deposition Method. *Appl. Catal. A: General* **2015**, *503*, 135−146.

(621) Hu, S.; Shima, T.; Hou, Z. Hydrodeoxygenative Cyclotetramerization of Carbon Monoxide by a Trinuclear Titanium

Polyhydride Complex. *J. American Chem. Soc.* **2020**, *142*, 19889−19894.

(622) Wei, Z.; Li, Q.; Cheng, Y.; Dong, M.; Zhang, Z.; Zhu, X.; Liu, Y.; Sun, Y. Low Loading of Core/Tio2 for Efficient Hydrodeoxygenation of Levulinic Acid to Γ-Valerolactone. *ACS Sus. Chem. Eng.* **2021**, *9*, 10882−10891.

(623) Li, W.; Geng, W.; Liu, L.; Shang, Q.; Liu, L.; Kong, X. In Situ-Generated Co Embedded in N-Doped Carbon Hybrids as Robust Catalysts for the Upgrading of Levulinic Acid in Aqueous Phase. *Sus. Energy & Fuels* **2020**, *4*, 2043−2054.

(624) Zhao, H.; Hao, J.; Ban, Y.; Sha, Y.; Zhou, H.; Liu, Q. Novel and Efficient Cobalt Catalysts Synthesized by One-Step Solution Phase Reduction for the Conversion of Biomass Derived Ethyl Levulinate. *Catal. Today* **2019**, *319*, 145−154.

(625) Novodárszki, G.; Solt, H. E.; Valyon, J.; Lónyi, F.; Hancsók, J.; Deka, D.; Tuba, R.; Mihályi, M. R. Selective Hydroconversion of Levulinic Acid to Γ-Valerolactone or 2-Methyltetrahydrofuran over Silica-Supported Cobalt Catalysts. *Catal. Sci. Technol.* **2019**, *9*, 2291−2304.

(626) Liu, X.; Li, Z. Efficient Transfer Hydrogenation of Levulinic Acid (La) to Γ-Valerolactone (Gvl) over Ni/Nio-Mc (Mc = Mesoporous Carbon). *Sus. Energy & Fuels* **2021**, *5*, 3312−3320.

(627) Zada, B.; Zhu, R.; Wang, B.; Liu, J.; Deng, J.; Fu, Y. A Practical and Concise Homogeneous Nickel Catalyst for Efficient Solvent-Free Synthesis of Γ-Valerolactone. *Green Chem.* **2020**, *22*, 3427−3432.

(628) Soszka, E.; Reijneveld, H. M.; Jędrzejczyk, M.; Rzeźnicka, I.; Grams, J.; Ruppert, A. M. Chlorine Influence on Palladium Doped Nickel Catalysts in Levulinic Acid Hydrogenation with Formic Acid as Hydrogen Source. *ACS Sus. Chem. Eng.* **2018**, *6*, 14607−14613.

(629) Lopez-Aguado, C.; Paniagua, M.; Melero, J. A.; Iglesias, J.; Juarez, P.; Granados, M. L.; Morales, G. Stable Continuous Production of Gamma-Valerolactone from Biomass-Derived Levulinic Acid over Zr-Al-Beta Zeolite Catalyst. *Catalysts* **2020**, *10*, 678.

(630) Vásquez, P. B.; Tabanelli, T.; Monti, E.; Albonetti, S.; Bonincontro, D.; Dimitratos, N.; Cavani, F. Gas-Phase Catalytic Transfer Hydrogenation of Methyl Levulinate with Ethanol over Zro2. *ACS Sus. Chem. Eng.* **2019**, *7*, 8317−8330.

(631) Meng, Z.; Liu, Y.; Yang, G.; Cao, Y.; Wang, H.; Peng, F.; Liu, P.; Yu, H. Electron-Rich Ruthenium on Nitrogen-Doped Carbons Promoting Levulinic Acid Hydrogenation to Γ-Valerolactone: Effect of Metal-Support Interaction. *ACS Sus. Chem. Eng.* **2019**, *7*, 16501−16510.

(632) Gundekari, S.; Srinivasan, K. Hydrous Ruthenium Oxide: A New Generation Remarkable Catalyst Precursor for Energy Efficient and Sustainable Production of Γ-Valerolactone from Levulinic Acid in Aqueous Medium. *Appl. Catal. A: General* **2019**, *569*, 117−125.

(633) Lin, Z. Z.; Luo, M. T.; Zhang, Y. D.; Wu, X. X.; Fu, Y. H.; Zhang, F. M.; Zhu, W. D. Coupling Ru Nanoparticles and Sulfonic Acid Moieties on Single Mil-101 Microcrystals for Upgrading Methyl Levulinate into Gamma-Valerolactone. *Appl. Catal. A: General* **2018**, *563*, 54−63.

(634) Kumar, A.; Srivastava, R. Cepo4, a Multi-Functional Catalyst for Carbohydrate Biomass Conversion: Production of 5-Hydroxymethylfurfural, 2,5-Diformylfuran, and Γ-Valerolactone. *Sus. Energy & Fuels* **2019**, *3*, 2475−2489.

(635) Feng, H.-J.; Li, X.-C.; Qian, H.; Zhang, Y.-F.; Zhang, D.-H.; Zhao, D.; Hong, S.-G.; Zhang, N. Efficient and Sustainable Hydrogenation of Levulinic-Acid to Gamma-Valerolactone in Aqueous Solution over Acid-Resistant Cepo4/Co2p Catalysts. *Green Chem.* **2019**, *21*, 1743−1756.

(636) Al-Naji, M.; Popova, M.; Chen, Z.; Wilde, N.; Glaser, R. Aqueous-Phase Hydrogenation of Levulinic Acid Using Formic Acid as a Sustainable Reducing Agent over Pt Catalysts Supported on Mesoporous Zirconia. *ACS Sus. Chem. Eng.* **2020**, *8*, 393−402.

(637) Tang, B.; Li, S.; Song, W.-C.; Yang, E.-C.; Zhao, X.-J.; Guan, N.; Li, L. Hierarchical Fau-Type Hafnosilicate Zeolite as a Robust Lewis Acid Catalyst for Catalytic Transfer Hydrogenation. *ACS Sus. Chem. Eng.* **2019**, *7*, 16329−16343.

(638) Pendem, S.; Mondal, I.; Shrotri, A.; Rao, B. S.; Lingaiah, N.; Mondal, J. Unraveling the Structural Properties and Reactivity Trends of Cu-Ni Bimetallic Nanoalloy Catalysts for Biomass- Derived Levulinic Acid Hydrogenation. *Sus. Energy & Fuels* **2018**, *2*, 1516−1529.

(639) Bui, L.; Luo, H.; Gunther, W. R.; Román-Leshkov, Y. Domino Reaction Catalyzed by Zeolites with Brønsted and Lewis Acid Sites for the Production of Γ-Valerolactone from Furfural. *Angew. Chem., Int. Ed.* **2013**, *52*, 8022−8025.

(640) Tan, J.; Liu, Y.; Li, M.; Li, H.; Yang, S. One-Step Catalytic Upgrading of Bio-Based Furfural to Γ-Valerolactone Actuated by Coordination Organophosphate-Hf Polymers. *Sus. Energy & Fuels* **2022**, *6*, 484−501.

(641) Tang, B.; Li, S.; Song, W.-C.; Li, Y.; Yang, E.-C. One-Pot Transformation of Furfural into Γ-Valerolactone Catalyzed by a Hierarchical Hf-Al-Usy Zeolite with Balanced Lewis and Brønsted Acid Sites. *Sus. Energy & Fuels* **2021**, *5*, 4724−4735.

(642) Karnjanakom, S.; Bayu, A.; Maneechakr, P.; Samart, C.; Kongparakul, S.; Guan, G. Simultaneous Assistance of Molecular Oxygen and Mesoporous So3h-Alumina for a Selective Conversion of Biomass-Derived Furfural to Γ-Valerolactone without an External Addition of H2. *Sus. Energy & Fuels* **2021**, *5*, 4041−4052.

(643) Srinivasa Rao, B.; Yogita; Dhana Lakshmi, D.; Kumari, P. K.; Lingaiah, N. Influence of Metal Oxide and Heteropoly Tungstate Location in Mesoporous Silica Towards Catalytic Transfer Hydrogenation of Furfural to Γ-Valerolactone. *Sus. Energy & Fuels* **2021**, *5*, 3719−3728.

(644) Li, W.; Li, M.; Liu, H.; Jia, W.; Yu, X.; Wang, S.; Zeng, X.; Sun, Y.; Wei, J.; Tang, X.; et al. Domino Transformation of Furfural to Γ-Valerolactone over Sapo-34 Zeolite Supported Zirconium Phosphate Catalysts with Tunable Lewis and Brønsted Acid Sites. *Mol. Catal.* **2021**, *506*, 111538.

(645) Morandi, S.; Manzoli, M.; Chan-Thaw, C. E.; Bonelli, B.; Stucchi, M.; Prati, L.; Störmer, H.; Wang, W.; Wang, D.; Pabel, M.; et al. Unraveling the Effect of Zro2Modifiers on the Nature of Active Sites on Auru/Zro2 Catalysts for Furfural Hydrogenation. *Sus. Energy & Fuels* **2020**, *4*, 1469−1480.

(646) Chen, T. N.; Qin, Z. F.; Qi, Y. Q.; Deng, T. S.; Ge, X. J.; Wang, J. G.; Hou, X. L. Degradable Polymers from Ring-Opening Polymerization of Alpha-Angelica Lactone, a Five-Membered Unsaturated Lactone. *Polym. Chem.* **2011**, *2*, 1190−1194.

(647) Dell'Acqua, A.; Stadler, B. M.; Kirchhecker, S.; Tin, S.; de Vries, J. G. Scalable Synthesis and Polymerisation of a Beta-Angelica Lactone Derived Monomer. *Green Chem.* **2020**, *22*, 5267−5273.

(648) Sun, D. L.; Takahashi, Y.; Yamada, Y.; Sato, S. Efficient Formation of Angelica Lactones in a Vapor-Phase Conversion of Levulinic Acid. *Appl. Catal. A: General* **2016**, *526*, 62−69.

(649) Xin, J.; Zhang, S.; Yan, D.; Ayodele, O.; Lu, X.; Wang, J. Formation of C-C Bonds for the Production of Bio-Alkanes under Mild Conditions. *Green Chem.* **2014**, *16*, 3589−3595.

(650) Mascal, M.; Dutta, S.; Gandarias, I. Hydrodeoxygenation of the Angelica Lactone Dimer, a Cellulose-Based Feedstock: Simple, High-Yield Synthesis of Branched C7-C10 Gasoline-Like Hydrocarbons. *Angew. Chem., Int. Ed.* **2014**, *53*, 1854−1857.

(651) Kumaravel, S.; Thiripuranthagan, S.; Erusappan, E. Wo3/Al-Hzsm-5 Catalysts for Effective Catalytic Conversion of Biomass-Derived Levulinic Acid to Angelica Lactones. *Emerg. Mater.* **2021**, *4*, 791−802.

(652) Antunes, M. M.; Lima, S.; Neves, P.; Magalhaes, A. L.; Fazio, E.; Fernandes, A.; Neri, F.; Silva, C. M.; Rocha, S. M.; Eiro, M. F. R.; et al. One-Pot Conversion of Furfural to Useful Bio-Products in the Presence of a Sn,Al-Containing Zeolite Beta Catalyst Prepared Via Post-Synthesis Routes. *J. Catal.* **2015**, *329*, 522−537.

(653) Bozell, J. J.; Petersen, G. R. Technology Development for the Production of Biobased Products from Biorefinery Carbohydrates—the Us Department of Energy's "Top 10" Revisited. *Green Chem.* **2010**, *12*, 539−554.

(654) Yamaguchi, S.; Matsuo, T.; Motokura, K.; Sakamoto, Y.; Miyaji, A.; Baba, T. Mechanistic Studies on the Cascade Conversion

of 1,3-Dihydroxyacetone and Formaldehyde into A-Hydroxy-Γ-Butyrolactone. *ChemSusChem* **2015**, *8*, 853−860.

(655) Liu, X. Q.; Wang, M. X.; Li, Z. C.; Li, F. M. Synthesis and Ring-Opening Polymerization of Alpha-Chloromethyl-Alpha-Methyl-Beta-Propiolactone. *Macromol. Chem. Phys.* **1999**, *200*, 468−473.

(656) Peres, R.; Lenz, R. W. Synthesis and Polymerization of (R,S)-Beta-Pentyl-Beta-Propiolactone. *Macromolecules* **1993**, *26*, 6697−6701.

(657) Dunn, E. W.; Lamb, J. R.; LaPointe, A. M.; Coates, G. W. Carbonylation of Ethylene Oxide to Beta-Propiolactone: A Facile Route to Poly(3-Hydroxypropionate) and Acrylic Acid. *ACS Catal.* **2016**, *6*, 8219−8223.

(658) Faveere, W. H.; Van Praet, S.; Vermeeren, B.; Dumoleijn, K. N. R.; Moonen, K.; Taarning, E.; Sels, B. F. Toward Replacing Ethylene Oxide in a Sustainable World: Glycolaldehyde as a Bio-Based C2 Platform Molecule. *Angew. Chem., Int. Ed.* **2021**, *60*, 12204−12223.

(659) Xie, Z. Y.; Deng, J.; Fu, Y. W(Otf)(6)-Catalyzed Synthesis of Gamma-Lactones by Ring Contraction of Macrolides or Ring Closing of Terminal Hydroxyfatty Acids in Ionic Liquid. *ChemSusChem* **2018**, *11*, 2332−2339.

(660) Bonneau, G.; Peru, A. A. M.; Flourat, A. L.; Allais, F. Organic Solvent- and Catalyst-Free Baeyer-Villiger Oxidation of Levoglucosenone and Dihydrolevoglucosenone (Cyrene (R)): A Sustainable Route to (S)-Gamma-Hydroxymethyl-Alpha,Beta-Butenolide and (S)-Gamma-Hydroxymethyl-Gamma-Butyrolactone. *Green Chem.* **2018**, *20*, 2455−2458.

(661) Kiziltas, A.; Gardner, D. J.; Han, Y.; Yang, H.-S. Mechanical Properties of Microcrystalline Cellulose (Mcc) Filled Engineering Thermoplastic Composites. *J. Polym. Environ.* **2014**, *22*, 365−372.

(662) Yan, C.; Fraga-Dubreuil, J.; Garcia-Verdugo, E.; Hamley, P. A.; Poliakoff, M.; Pearson, I.; Coote, A. S. The Continuous Synthesis of Epsilon-Caprolactam from 6-Aminocapronitrile in High-Temperature Water. *Green Chem.* **2008**, *10*, 98−103.

(663) Cheng, J.; Chen, P.; Song, A.; Wang, D.; Wang, Q. Expanding Lysine Industry: Industrial Biomanufacturing of Lysine and Its Derivatives. *J. Ind. Microbiol. Biotechnol.* **2018**, *45*, 719−734.

(664) Sebastian, J.; Zheng, M.; Jiang, Y.; Zhao, Y.; Wang, H.; Song, Z.; Li, X.; Pang, J.; Zhang, T. One-Pot Conversion of Lysine to Caprolactam over Ir/H-Beta Catalysts. *Green Chem.* **2019**, *21*, 2462−2468.

(665) Cespi, D.; Passarini, F.; Vassura, I.; Cavani, F. Butadiene from Biomass, a Life Cycle Perspective to Address Sustainability in the Chemical Industry. *Green Chem.* **2016**, *18*, 1625−1638.

(666) Morrow, N. L. The Industrial Production and Use of 1,3-Butadiene. *Environ. Health Perspect.* **1990**, *86*, 7−8.

(667) Kumalaputri, A. J.; Randolph, C.; Otten, E.; Heeres, H. J.; Deuss, P. J. Lewis Acid Catalyzed Conversion of 5-Hydroxymethylfurfural to 1,2,4-Benzenetriol, an Overlooked Biobased Compound. *ACS Sus. Chem. Eng.* **2018**, *6*, 3419−3425.

(668) Liu, P.; Zhang, H.; Lv, M.; Hu, M.; Li, Z.; Gao, C.; Xu, P.; Ma, C. Enzymatic Production of 5-Aminovalerate from L-Lysine Using L-Lysine Monooxygenase and 5-Aminovaleramide Amidohydrolase. *Sci. Rep.* **2015**, *4*, 5657.

(669) Park, S. J.; Oh, Y. H.; Noh, W.; Kim, H. Y.; Shin, J. H.; Lee, E. G.; Lee, S.; David, Y.; Baylon, M. G.; Song, B. K.; et al. High-Level Conversion of L-Lysine into 5-Aminovalerate That Can Be Used for Nylon 6,5 Synthesis. *Biotechnol. J.* **2014**, *9*, 1322−1328.

(670) Zhang, J.; Barajas, J. F.; Burdu, M.; Wang, G.; Baidoo, E. E.; Keasling, J. D. Application of an Acyl-Coa Ligase from Streptomyces Aizunensis for Lactam Biosynthesis. *ACS Synth. Biol.* **2017**, *6*, 884−890.

(671) Haupka, C.; Delépine, B.; Irla, M.; Heux, S.; Wendisch, V. F. Flux Enforcement for Fermentative Production of 5-Aminovalerate and Glutarate by Corynebacterium Glutamicum. *Catalysts* **2020**, *10*, 1065.

(672) Jorge, J. M. P.; Pérez-García, F.; Wendisch, V. F. A New Metabolic Route for the Fermentative Production of 5-Aminovalerate from Glucose and Alternative Carbon Sources. *Bioresour. Technol.* **2017**, *245*, 1701−1709.

(673) Pukin, A. V.; Boeriu, C. G.; Scott, E. L.; Sanders, J. P. M.; Franssen, M. C. R. An Efficient Enzymatic Synthesis of 5-Aminovaleric Acid. *J. Mol. Catal. B: Enzymatic* **2010**, *65*, 58−62.

(674) Cheng, J.; Tu, W.; Luo, Z.; Liang, L.; Gou, X.; Wang, X.; Liu, C.; Zhang, G. Coproduction of 5-Aminovalerate and Δ-Valerolactam for the Synthesis of Nylon 5 from L-Lysine in Escherichia Coli. *Front. Bioeng. Biotechnol.* **2021**, *9*, 726126.

(675) Eckermann, S.; Schröder, G.; Schmidt, J.; Strack, D.; Edrada, R. A.; Helariutta, Y.; Elomaa, P.; Kotilainen, M.; Kilpeläinen, I.; Proksch, P.; et al. New Pathway to Polyketides in Plants. *Nature* **1998**, *396*, 387−390.

(676) Chen, B.; Xie, Z.; Peng, F.; Li, S.; Yang, J.; Wu, T.; Fan, H.; Zhang, Z.; Hou, M.; Li, S.; et al. Production of Piperidine and Δ-Lactam Chemicals from Biomass-Derived Triacetic Acid Lactone. *Angew. Chem., Int. Ed.* **2021**, *60*, 14405−14409.

(677) Liu, X. L.; Xu, Y. J.; Wu, Z. Q.; Chen, H. Poly(N-Vinylpyrrolidone)-Modified Surfaces for Biomedical Applications. *Macromol. Biosci.* **2013**, *13*, 147−154.

(678) Touchy, A. S.; Hakim Siddiki, S. M. A.; Kon, K.; Shimizu, K.-i. Heterogeneous Pt Catalysts for Reductive Amination of Levulinic Acid to Pyrrolidones. *ACS Catal.* **2014**, *4*, 3045−3050.

(679) Wu, P. D.; Li, H.; Fang, Z. Synergistic Catalysis of Co-Zr/Cnx Bimetallic Nanoparticles Enables Reductive Amination of Biobased Levulinic Acid. *Adv. Sustainable Sys.* **2022**, *6*, 2100321.

(680) Huang, Y.-B.; Dai, J.-J.; Deng, X.-J.; Qu, Y.-C.; Guo, Q.-X.; Fu, Y. Ruthenium-Catalyzed Conversion of Levulinic Acid to Pyrrolidines by Reductive Amination. *ChemSusChem* **2011**, *4*, 1578−1581.

(681) Wang, S.; Huang, H.; Bruneau, C.; Fischmeister, C. Selective and Efficient Iridium Catalyst for the Reductive Amination of Levulinic Acid into Pyrrolidones. *ChemSusChem* **2017**, *10*, 4150−4154.

(682) Ledoux, A.; Sandjong Kuigwa, L.; Framery, E.; Andrioletti, B. A Highly Sustainable Route to Pyrrolidone Derivatives - Direct Access to Biosourced Solvents. *Green Chem.* **2015**, *17*, 3251−3254.

(683) Mürtz, S. D.; Kurig, N.; Holzhäuser, F. J.; Palkovits, R. Reviving Electrocatalytic Reductive Amination: A Sustainable Route from Biogenic Levulinic Acid to 1,5-Dimethyl-2-Pyrrolidone. *Green Chem.* **2021**, *23*, 8428−8433.

(684) Louven, Y.; Haus, M. O.; Konrad, M.; Hofmann, J. P.; Palkovits, R. Efficient Palladium Catalysis for the Upgrading of Itaconic and Levulinic Acid to 2-Pyrrolidones Followed by Their Vinylation into Value-Added Monomers. *Green Chem.* **2020**, *22*, 4532−4540.

(685) Liu, C. L.; Zhao, L.; Yu, G. H. The Dominant Glutamic Acid Metabolic Flux to Produce Gamma-Amino Butyric Acid over Proline in Nicotiana Tabacum Leaves under Water Stress Relates to Its Significant Role in Antioxidant Activity. *J. Integ. Plant Biol.* **2011**, *53*, 608−618.

(686) Lammens, T. M.; Franssen, M. C. R.; Scott, E. L.; Sanders, J. P. M. Synthesis of Biobased N-Methylpyrrolidone by One-Pot Cyclization and Methylation of Γ-Aminobutyric Acid. *Green Chem.* **2010**, *12*, 1430−1436.

(687) De Schouwer, F.; Adriaansen, S.; Claes, L.; De Vos, D. E. Bio-Based N-Alkyl-2-Pyrrolidones by Pd-Catalyzed Reductive N-Alkylation and Decarboxylation of Glutamic Acid. *Green Chem.* **2017**, *19*, 4919−4929.

(688) Chae, T. U.; Ko, Y.-S.; Hwang, K.-S.; Lee, S. Y. Metabolic Engineering of Escherichia Coli for the Production of Four-, Five- and Six-Carbon Lactams. *Metab. Eng.* **2017**, *41*, 82−91.

(689) Salehi, M. M.; Ataeefard, M. Micro Powder Poly Lactic Acid/Carbon Black Composite as a Bio Printing Ink. *J. Comp. Mater.* **2019**, *53*, 2407−2414.

(690) Santoro, M.; Shah, S. R.; Walker, J. L.; Mikos, A. G. Poly(Lactic Acid) Nanofibrous Scaffolds for Tissue Engineering. *Adv. Drug Del. Reviews* **2016**, *107*, 206−212.

(691) Vergnol, G.; Ginsac, N.; Rivory, P.; Meille, S.; Chenal, J.-M.; Balvay, S.; Chevalier, J.; Hartmann, D. J. In Vitro and in Vivo

Evaluation of a Polylactic Acid-Bioactive Glass Composite for Bone Fixation Devices. *J. Biomed. Mater. Res. Part B Appl. Biomater.* **2016**, *104*, 180−191.

(692) Van Wouwe, P.; Dusselier, M.; Vanleeuw, E.; Sels, B. Lactide Synthesis and Chirality Control for Polylactic Acid Production. *ChemSusChem* **2016**, *9*, 907−921.

(693) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. Controlled Ring-Opening Polymerization of Lactide and Glycolide. *Chem. Rev.* **2004**, *104*, 6147−6176.

(694) Marianou, A. A.; Michailof, C. C.; Ipsakis, D.; Triantafyllidis, K.; Lappas, A. A. Cellulose Conversion into Lactic Acid over Supported Hpa Catalysts. *Green Chem.* **2019**, *21*, 6161−6178.

(695) Abdel-Rahman, M. A.; Tashiro, Y.; Sonomoto, K. Recent Advances in Lactic Acid Production by Microbial Fermentation Processes. *Biotechnol. Adv.* **2013**, *31*, 877−902.

(696) Morton, D.; Cole-Hamilton, D. J. Molecular Hydrogen Complexes in Catalysis: Highly Efficient Hydrogen Production from Alcoholic Substrates Catalysed by Ruthenium Complexes. *J. Chem. Soc., Chem. Commun.* **1988**, 1154−1156.

(697) Li, Y.; Nielsen, M.; Li, B.; Dixneuf, P. H.; Junge, H.; Beller, M. Ruthenium-Catalyzed Hydrogen Generation from Glycerol and Selective Synthesis of Lactic Acid. *Green Chem.* **2015**, *17*, 193−198.

(698) Lakshmanan, P.; Upare, P. P.; Le, N.-T.; Hwang, Y. K.; Hwang, D. W.; Lee, U. H.; Kim, H. R.; Chang, J.-S. Facile Synthesis of Ceo2-Supported Gold Nanoparticle Catalysts for Selective Oxidation of Glycerol into Lactic Acid. *Appl. Catal. A: General* **2013**, *468*, 260−268.

(699) Zhang, C.; Wang, T.; Liu, X.; Ding, Y. Selective Oxidation of Glycerol to Lactic Acid over Activated Carbon Supported Pt Catalyst in Alkaline Solution. *Chin. J. Catal.* **2016**, 37, 502−509.

(700) Cho, H. J.; Chang, C.-C.; Fan, W. Base Free, One-Pot Synthesis of Lactic Acid from Glycerol Using a Bifunctional Pt/Sn-Mfi Catalyst. *Green Chem.* **2014**, *16*, 3428−3433.

(701) Shen, Z.; Jin, F.; Zhang, Y.; Wu, B.; Kishita, A.; Tohji, K.; Kishida, H. Effect of Alkaline Catalysts on Hydrothermal Conversion of Glycerin into Lactic Acid. *Ind. Eng. Chem. Res.* **2009**, *48*, 8920−8925.

(702) Ramírez-López, C. A.; Ochoa-Gómez, J. R.; Fernández-Santos, M.; Gómez-Jiménez-Aberasturi, O.; Alonso-Vicario, A.; Torrecilla-Soria, J. Synthesis of Lactic Acid by Alkaline Hydrothermal Conversion of Glycerol at High Glycerol Concentration. *Ind. Eng. Chem. Res.* **2010**, *49*, 6270−6278.

(703) Li, L.; Shen, F.; Smith, R. L.; Qi, X. Quantitative Chemocatalytic Production of Lactic Acid from Glucose under Anaerobic Conditions at Room Temperature. *Green Chem.* **2017**, *19*, 76−81.

(704) Wang, Y.; Deng, W.; Wang, B.; Zhang, Q.; Wan, X.; Tang, Z.; Wang, Y.; Zhu, C.; Cao, Z.; Wang, G.; et al. Chemical Synthesis of Lactic Acid from Cellulose Catalysed by Lead(Ii) Ions in Water. *Nat. Commun.* **2013**, *4*, 2141.

(705) Tang, Z.; Deng, W.; Wang, Y.; Zhu, E.; Wan, X.; Zhang, Q.; Wang, Y. Transformation of Cellulose and Its Derived Carbohydrates into Formic and Lactic Acids Catalyzed by Vanadyl Cations. *ChemSusChem* **2014**, *7*, 1557−1567.

(706) Lei, X.; Wang, F.-F.; Liu, C.-L.; Yang, R.-Z.; Dong, W.-S. One-Pot Catalytic Conversion of Carbohydrate Biomass to Lactic Acid Using an Ercl3 Catalyst. *Appl. Catal. A: General* **2014**, *482*, 78−83.

(707) Deng, W.; Wang, P.; Wang, B.; Wang, Y.; Yan, L.; Li, Y.; Zhang, Q.; Cao, Z.; Wang, Y. Transformation of Cellulose and Related Carbohydrates into Lactic Acid with Bifunctional Al(Iii)-Sn(Ii) Catalysts. *Green Chem.* **2018**, *20*, 735−744.

(708) Wang, F.-F.; Liu, J.; Li, H.; Liu, C.-L.; Yang, R.-Z.; Dong, W.-S. Conversion of Cellulose to Lactic Acid Catalyzed by Erbium-Exchanged Montmorillonite K10. *Green Chem.* **2015**, *17*, 2455−2463.

(709) Bielawski, C. W.; Grubbs, R. H. Living Ring-Opening Metathesis Polymerization. *Prog. Polym. Sci. (Oxford)* **2007**, *32*, 1−29.

(710) Strick, B. F.; Delferro, M.; Geiger, F. M.; Thomson, R. J. Investigations into Apopinene as a Biorenewable Monomer for Ring-Opening Metathesis Polymerization. *ACS Sus. Chem. Eng.* **2015**, *3*, 1278−1281.

(711) Yarolimek, M. R.; Bookbinder, H. R.; Coia, B. M.; Kennemur, J. G. Ring-Opening Metathesis Polymerization of Δ-Pinene: Well-Defined Polyolefins from Pine Sap. *ACS Macro Lett.* **2021**, *10*, 760−766.

(712) Yarolimek, M. R.; Coia, B. M.; Bookbinder, H. R.; Kennemur, J. G. Investigating the Effect of A-Pinene on the Romp of Δ-Pinene. *Polym. Chem.* **2021**, *12*, 5048−5058.

(713) Grau, E.; Mecking, S. Polyterpenes by Ring Opening Metathesis Polymerization of Caryophyllene and Humulene. *Green Chem.* **2013**, *15*, 1112−1115.

(714) Medeiros, A. M. M. S.; Le Coz, C.; Grau, E. Caryophyllene as a Precursor of Cross-Linked Materials. *ACS Sus. Chem. Eng.* **2020**, *8*, 4451−4456.

(715) Janiak, C.; Lassahn, P. G. The Vinyl Homopolymerization of Norbornene. *Macromol. Rap. Commun.* **2001**, *22*, 479−493.

(716) Bai, Y.; De bruyn, M.; Clark, J. H.; Dodson, J. R.; Farmer, T. J.; Honoré, M.; Ingram, I. D. V.; Naguib, M.; Whitwood, A. C.; North, M. Ring Opening Metathesis Polymerisation of a New Bio-Derived Monomer from Itaconic Anhydride and Furfuryl Alcohol. *Green Chem.* **2016**, *18*, 3945−3948.

(717) Lawrenson, S. B.; Hart, S.; Ingram, I. D. V.; North, M.; Parker, R. R.; Whitwood, A. C. Ring-Opening Metathesis Polymerization of Tertiary Amide Monomers Derived from a Biobased Oxanorbornene. *ACS Sus. Chem. Eng.* **2018**, *6*, 9744−9752.

(718) Fang, L.; Zhou, J.; Tao, Y.; Wang, Y.; Chen, X.; Chen, X.; Hou, J.; Sun, J.; Fang, Q. Low Dielectric Fluorinated Polynorbornene with Good Thermostability and Transparency Derived from a Biobased Allylphenol (Eugenol). *ACS Sus. Chem. Eng.* **2019**, *7*, 4078−4086.

(719) Dell'Acqua, A.; Stadler, B. M.; Kirchhecker, S.; Tin, S.; de Vries, J. G. Scalable Synthesis and Polymerisation of a Β-Angelica Lactone Derived Monomer. *Green Chem.* **2020**, *22*, 5267−5273.

(720) Debsharma, T.; Behrendt, F. N.; Laschewsky, A.; Schlaad, H. Ring-Opening Metathesis Polymerization of Biomass-Derived Levoglucosenol. *Angew. Chem., Int. Ed.* **2019**, *58*, 6718−6721.

(721) Hoogenboom, R. Poly(2-Oxazoline)S: A Polymer Class with Numerous Potential Applications. *Angew. Chem., Int. Ed.* **2009**, *48*, 7978−7994.

(722) Glassner, M.; Vergaelen, M.; Hoogenboom, R. Poly(2-Oxazoline)S: A Comprehensive Overview of Polymer Structures and Their Physical Properties. *Polym. Internat.* **2018**, *67*, 32−45.

(723) Hoogenboom, R. Poly(2-Oxazoline)S Based on Fatty Acids. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 59−71.

(724) Kempe, K.; Hoogenboom, R.; Schubert, U. S. A Green Approach for the Synthesis and Thiol-Ene Modification of Alkene Functionallized Poly(2-Oxazoline)S. *Macromol. Rap. Commun.* **2011**, *32*, 1484−1489.

(725) Cai, G.; Litt, M. H. Synthesis and Characterization of Poly(N-Acyl or N-Aroyl Ethylenimines) Containing Various Pendant Functional Groups. Iii. Copolymers with Pendant Epoxy and Imidazole Groups. *J. Polym. Sci. A: Polym. Chem.* **1996**, *34*, 2701−2709.

(726) Cai, G.; Litt, M. H. Poly(N-Acylethylenimine) Copolymers Containing Pendant Pentamethyldisiloxanyl Groups. Ii. Thermal Behavior and X-Ray Diffraction Study. *J. Polym. Sci. A: Polym. Chem.* **1992**, *30*, 659−669.

(727) Kim, J.; Waldron, C.; Cattoz, B.; Becer, C. R. An ϵ-Caprolactone-Derived 2-Oxazoline Inimer for the Synthesis of Graft Copolymers. *Polym. Chem.* **2020**, *11*, 6847−6852.

(728) Schuler, E.; Demetriou, M.; Shiju, N. R.; Gruter, G. J. M. Towards Sustainable Oxalic Acid from Co2 and Biomass. *ChemSusChem* **2021**, *14*, 3636−3664.

(729) Riemenschneider, W.; Raines, R. T. *Ullmann's Encuclopedia of Industrial Chemistry*; Wiley-VHC, 2012.

(730) Sawada, H.; Murakami, T. Oxalic Acid. *Kirk-Othmer Encyclopedia of Chemical Technology* **2000**, *17*, 882−902.

(731) Wan, Y.; Lee, J.-M. Toward Value-Added Dicarboxylic Acids from Biomass Derivatives Via Thermocatalytic Conversion. *ACS Catal.* **2021**, *11*, 2524−2560.

(732) Dube, S. K.; Vasudevan, P.; Khandelwal, B. L. Oxalic Acid Manufacture. *J. Chem. Technol. Biotechnol.* **1982**, *32*, 909−919.

(733) Othmer, D. F.; Gamer, C. H.; Jacobs, J. J. Oxalic Acid from Sawdust - Optimum Conditions for Manufacture. *Ind. Eng. Chem.* **1942**, *34*, 262−267.

(734) Mathew, M. D.; Gopal, M.; Banerjee, S. K. Preparation of Oxalic Acid from Jute Stick, an Agrowaste. *Agric. Wastes* **1984**, *11*, 47−59.

(735) Jiang, Z.; Zhang, Z.; Song, J.; Meng, Q.; Zhou, H.; He, Z.; Han, B. Metal-Oxide-Catalyzed Efficient Conversion of Cellulose to Oxalic Acid in Alkaline Solution under Low Oxygen Pressure. *ACS Sus. Chem. Eng.* **2016**, *4*, 305−311.

(736) Beverskog, B.; Puigdomenech, I. Revised Pourbaix Diagrams for Copper at 25 to 300°C. *J. Electrochem. Soc.* **1997**, *144*, 3476−3483.

(737) Cai, J.; Ma, H.; Zhang, J.; Du, Z.; Huang, Y.; Gao, J.; Xu, J. Catalytic Oxidation of Glycerol to Tartronic Acid over Au/Hy Catalyst under Mild Conditions. *Chin. J. Catal.* **2014**, *35*, 1653−1660.

(738) Ventura, M.; Williamson, D.; Lobefaro, F.; Jones, M. D.; Mattia, D.; Nocito, F.; Aresta, M.; Dibenedetto, A. Sustainable Synthesis of Oxalic and Succinic Acid through Aerobic Oxidation of C6 Polyols under Mild Conditions. *ChemSusChem* **2018**, *11*, 1073−1081.

(739) Kaiser, U.; Heitz, E. Zum Mechanismus Der Elektrochemischen Dimerisierung Von Co2 Zu Oxalsäure. *Ber. Bunsenges. Phys. Chem.* **1973**, *77*, 818−823.

(740) Gressin, J.; Michelet, D.; Nadjo, L.; Saveant, J. Electrochemical Reduction of Carbon Dioxide in Weakly Protic Medium. *Chem. Inf.-Dienst* **1979**, *10*, 10.

(741) Amatore, C.; Saveant, J. M. Mechanism and Kinetic Characteristics of the Electrochemical Reduction of Carbon Dioxide in Media of Low Proton Availability. *J. American Chem. Soc.* **1981**, *103*, 5021−5023.

(742) Fischer, J.; Lehmann, T.; Heitz, E. The Production of Oxalic Acid from Co2 and H2o. *J. Appl. Electrochem.* **1981**, *11*, 743−750.

(743) Paris, A. R.; Bocarsly, A. B. High-Efficiency Conversion of Co2 to Oxalate in Water Is Possible Using a Cr-Ga Oxide Electrocatalyst. *ACS Catal.* **2019**, *9*, 2324−2333.

(744) Schuler, E.; Ermolich, P. A.; Shiju, N. R.; Gruter, G.-J. M. Monomers from Co2: Superbases as Catalysts for Formate-to-Oxalate Coupling. *ChemSusChem* **2021**, *14*, 1517−1523.

(745) Becker, J. Y.; Vainas, B.; Eger, R.; Kaufman, L. Electrocatalytic Reduction of Co2 to Oxalate by Ag and Pd Porphyrins. *J. Chem. Soc., Chem. Commun.* **1985**, *21*, 1471−1472.

(746) Kushi, Y.; Nagao, H.; Nishioka, T.; Isobe, K.; Tanaka, K. Remarkable Decrease in Overpotential of Oxalate Formation in Electrochemical Co2 Reduction by a Metal-Sulfide Cluster. *J. Chem. Soc., Chem. Commun.* **1995**, 1223−1224.

(747) Kushi, Y.; Nagao, H.; Nishioka, T.; Isobe, K.; Tanaka, K. Oxalate Formation in Electrochemical Co2 Reduction Catalyzed by Rhodium-Sulfur Cluster. *Chem. Lett.* **1994**, *23*, 2175−2178.

(748) Evans, W. J.; Seibel, C. A.; Ziller, J. W. Organosamarium-Mediated Transformations of Co2 and Cos: Monoinsertion and Disproportionation Reactions and the Reductive Coupling of Co2 to [O2cco2]2. *Inorg. Chem.* **1998**, *37*, 770−776.

(749) Angamuthu, R.; Byers, P.; Lutz, M.; Spek, A. L.; Bouwman, E. Electrocatalytic Co2 Conversion to Oxalate by a Copper Complex. *Science* **2010**, *327*, 313−315.

(750) Senthil Kumar, R.; Senthil Kumar, S.; Anbu Kulandainathan, M. Highly Selective Electrochemical Reduction of Carbon Dioxide Using Cu Based Metal Organic Framework as an Electrocatalyst. *Electrochem. Commun.* **2012**, *25*, 70−73.

(751) Cohn, G. Oxalic Acid. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 1929; pp 426−429.

(752) Horn, O. Ullmanns Enzyklopädie Der Technischen Chemie. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 1953; pp 73−78.

(753) Weise, J.; Rieche, F.; Barth, A. Process of Making Formates. US 820159, 1906.

(754) Hietala, J.; Vuori, A.; Johnsson, P.; Pollari, I. I.; Reutemann, W.; Kieczka, H. Alkali Formates. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2016; pp 335−340.

(755) Lundsted, L. G. The Hydrogenation of Sodium Bicarbonate to Sodium Formate. *J. American Chem. Soc.* **1949**, *71*, 323−324.

(756) Kumar, A.; Semwal, S.; Choudhury, J. Catalytic Conversion of Co2 to Formate with Renewable Hydrogen Donors: An Ambient-Pressure and H2-Independent Strategy. *ACS Catal.* **2019**, *9*, 2164−2168.

(757) Kamble, S. P.; Kalshetti, R. G.; Vaithiyanathan, V. Metal Catalyzed Process for Reduction of Co2 to Sodium Formate and Formic Acid. WO 2016/024293A1, 2016.

(758) Hammer, N. I.; Sutton, S.; Delcamp, J.; Graham, J. D. Photocatalytic Water Splitting and Carbon Dioxide Reduction. In *Handbook of Climate Change Mitigation and Adaptation*; Chen, W.-Y., Suzuki, T., Lackner, M., Eds.; Springer International Publishing: Cham, 2017; pp 2709−2756.

(759) Rodrigues, R. R.; Boudreaux, C. M.; Papish, E. T.; Delcamp, J. H. Photocatalytic Reduction of Co2 to Co and Formate: Do Reaction Conditions or Ruthenium Catalysts Control Product Selectivity? *ACS Appl. Energy Mater.* **2019**, *2*, 37−46.

(760) Yaashikaa, P. R.; Senthil Kumar, P.; Varjani, S. J.; Saravanan, A. A Review on Photochemical, Biochemical and Electrochemical Transformation of Co2 into Value-Added Products. *J. CO2 Util.* **2019**, *33*, 131−147.

(761) Zhai, Q.; Xie, S.; Fan, W.; Zhang, Q.; Wang, Y.; Deng, W.; Wang, Y. Photocatalytic Conversion of Carbon Dioxide with Water into Methane: Platinum and Copper(I) Oxide Co-Catalysts with a Core-Shell Structure. *Angew. Chem., Int. Ed.* **2013**, *52*, 5776−5779.

(762) Zhou, H.; Guo, J.; Li, P.; Fan, T.; Zhang, D.; Ye, J. Leaf-Architectured 3d Hierarchical Artificial Photosynthetic System of Perovskite Titanates Towards Co2 Photoreduction into Hydrocarbon Fuels. *Sci. Rep.* **2013**, *3*, 1667.

(763) Merz, V.; Weith, W. Ueber Synthetische Oxalsäure. *Ber. Dtsch. Chem. Ges* **1882**, *15*, 1507−1513.

(764) Freidlin, L. K. Kinetics of Sodium Formate Thermal Decomposition. *Trans. All-Union Acad. Food Ind. named after Stalin* **1939**, 145−157.

(765) Bredt, O. P. C. Treatment of Formates of Metals of the Alkali-Earth Group. US 1622991, 1927.

(766) Huang, C.; Xu, T.; Zhang, Y.; Xue, Y.; Chen, G. Application of Electrodialysis to the Production of Organic Acids: State-of-the-Art and Recent Developments. *J. Memb. Sci.* **2007**, *288*, 1−12.

(767) Yazicigil, Z. Salt Splitting with Cation-Exchange Membranes. *Desalination* **2007**, *212*, 70−78.

(768) Scott, K. Process Intensification: An Electrochemical Perspective. *Renew. Sus. Energy Rev.* **2018**, *81*, 1406−1426.

(769) Yan, L.; Qi, X. Degradation of Cellulose to Organic Acids in Its Homogeneous Alkaline Aqueous Solution. *ACS Sus. Chem. Eng.* **2014**, *2*, 897−901.

(770) Liu, J.; Du, Z.; Yang, Y.; Lu, T.; Lu, F.; Xu, J. Catalytic Oxidative Decarboxylation of Malic Acid into Dimethyl Malonate in Methanol with Dioxygen. *ChemSusChem* **2012**, *5*, 2151−2154.

(771) Alonso-Fagúndez, N.; Granados, M. L.; Mariscal, R.; Ojeda, M. Selective Conversion of Furfural to Maleic Anhydride and Furan with Vox/Al2o3 Catalysts. *ChemSusChem* **2012**, *5*, 1984−1990.

(772) Guo, H.; Yin, G. Catalytic Aerobic Oxidation of Renewable Furfural with Phosphomolybdic Acid Catalyst: An Alternative Route to Maleic Acid. *J. Phys. Chem. C* **2011**, *115*, 17516−17522.

(773) Rodenas, Y.; Mariscal, R.; Fierro, J. L. G.; Martín Alonso, D.; Dumesic, J. A.; López Granados, M. Improving the Production of Maleic Acid from Biomass: Ts-1 Catalysed Aqueous Phase Oxidation of Furfural in the Presence of Γ-Valerolactone. *Green Chem.* **2018**, *20*, 2845−2856.

(774) Araji, N.; Madjinza, D. D.; Chatel, G.; Moores, A.; Jérôme, F.; De Oliveira Vigier, K. Synthesis of Maleic and Fumaric Acids from

Furfural in the Presence of Betaine Hydrochloride and Hydrogen Peroxide. *Green Chem.* **2017**, *19*, 98−101.

(775) Li, X.; Ho, B.; Lim, D. S. W.; Zhang, Y. Highly Efficient Formic Acid-Mediated Oxidation of Renewable Furfural to Maleic Acid with H2o2. *Green Chem.* **2017**, *19*, 914−918.

(776) Tirsoaga, A.; El Fergani, M.; Parvulescu, V. I.; Coman, S. M. Upgrade of 5-Hydroxymethylfurfural to Dicarboxylic Acids onto Multifunctional-Based Fe3o4@Sio2Magnetic Catalysts. *ACS Sus. Chem. Eng.* **2018**, *6*, 14292−14301.

(777) Pavarelli, G.; Velasquez Ochoa, J.; Caldarelli, A.; Puzzo, F.; Cavani, F.; Dubois, J.-L. A New Process for Maleic Anhydride Synthesis from a Renewable Building Block: The Gas-Phase Oxidehydration of Bio-1-Butanol. *ChemSusChem* **2015**, *8*, 2250−2259.

(778) Chatzidimitriou, A.; Bond, J. Q. Oxidation of Levulinic Acid for the Production of Maleic Anhydride: Breathing New Life into Biochemicals. *Green Chem.* **2015**, *17*, 4367−4376.

(779) Gao, Z.; Chen, W.; Chen, X.; Wang, D.; Yi, S. Study on the Isomerization of Maleic Acid to Fumaric Acid without Catalyst. *Bull. Korean Chem. Soc.* **2018**, *39*, 920−924.

(780) Maneechakr, P.; Karnjanakom, S. Catalytic Transformation of Furfural into Bio-Based Succinic Acid Via Ultrasonic Oxidation Using Β-Cyclodextrin-So3h Carbon Catalyst: A Liquid Biofuel Candidate. *Energy Convers. Manag.* **2017**, *154*, 299−310.

(781) Podolean, I.; Kuncser, V.; Gheorghe, N.; Macovei, D.; Parvulescu, V. I.; Coman, S. M. Ru-Based Magnetic Nanoparticles (Mnp) for Succinic Acid Synthesis from Levulinic Acid. *Green Chem.* **2013**, *15*, 3077−3082.

(782) Dutta, S.; Wu, L.; Mascal, M. Efficient, Metal-Free Production of Succinic Acid by Oxidation of Biomass-Derived Levulinic Acid with Hydrogen Peroxide. *Green Chem.* **2015**, *17*, 2335−2338.

(783) Rizescu, C.; Podolean, I.; Cojocaru, B.; Parvulescu, V. I.; Coman, S. M.; Albero, J.; Garcia, H. Rucl3 Supported on N-Doped Graphene as a Reusable Catalyst for the One-Step Glucose Oxidation to Succinic Acid. *ChemCatChem.* **2017**, *9*, 3314−3321.

(784) Wu, Q.; Wang, X.; Fu, S.; Hou, Z.; Zhao, F.; Chen, H.; Lei, S.; Zhang, H.; Bi, J.; Chai, W. Diphosphine Compound, Catalyst System Containing Diphosphine Compound and Application of Diphosphene. CN 112480170 A, 2021.

(785) Rao, V. N. M. Process for Preparing Butyrolactones and Butandiols. EP 0276012A3, 1988.

(786) Boussie, T. R.; Dias, E. L.; Fresco, Z. M.; Murphy, V. J.; Shoemaker, J. A. W.; Archer, R.; Jiang, H. Production of Adipic Acid and Derivatives from Carbohydrate-Containing Materials. US 2010/0317823 A1, 2010.

(787) Vardon, D. R.; Rorrer, N. A.; Salvachua, D.; Settle, A. E.; Johnson, C. W.; Menart, M. J.; Cleveland, N. S.; Ciesielski, P. N.; Steirer, K. X.; Dorgan, J. R.; et al. Cis,Cis-Muconic Acid: Separation and Catalysis to Bio-Adipic Acid for Nylon-6,6 Polymerization. *Green Chem.* **2016**, *18*, 3397−3413.

(788) Lyons, T. W.; Guironnet, D.; Findlater, M.; Brookhart, M. Synthesis of P-Xylene from Ethylene. *J. American Chem. Soc.* **2012**, *134*, 15708−15711.

(789) Peters, M. W.; Taylor, J. D.; Jenni, M.; Manzer, L. E.; Henton, D. E. Integrated Processs to Selectively Convert Renewable Isobutanol to P-Xylene. US 2011/0087000A1, 2011.

(790) Tao, L.; Yan, T.-H.; Li, W.; Zhao, Y.; Zhang, Q.; Liu, Y.-M.; Wright, M. M.; Li, Z.-H.; He, H.-Y.; Cao, Y. Toward an Integrated Conversion of 5-Hydroxymethylfurfural and Ethylene for the Production of Renewable P-Xylene. *Chem.* **2018**, *4*, 2212−2227.

(791) Song, S.; Zhang, J.; Gözaydın, G.; Yan, N. Production of Terephthalic Acid from Corn Stover Lignin. *Angew. Chem., Int. Ed.* **2019**, *58*, 4934−4937.

(792) Miller, K. K.; Zhang, P.; Nishizawa-Brennen, Y.; Frost, J. W. Synthesis of Biobased Terephthalic Acid from Cycloaddition of Isoprene with Acrylic Acid. *ACS Sus. Chem. Eng.* **2014**, *2*, 2053−2056.

(793) Colonna, M.; Berti, C.; Fiorini, M.; Binassi, E.; Mazzacurati, M.; Vannini, M.; Karanam, S. Synthesis and Radiocarbon Evidence of Terephthalate Polyesters Completely Prepared from Renewable Resources. *Green Chem.* **2011**, *13*, 2543−2548.

(794) Yu, H.; Kim, K.-A.; Kang, M. J.; Hwang, S. Y.; Cha, H. G. Carbon Support with Tunable Porosity Prepared by Carbonizing Chitosan for Catalytic Oxidation of 5-Hydroxylmethylfurfural. *ACS Sus. Chem. Eng.* **2019**, *7*, 3742−3748.

(795) Ait Rass, H.; Essayem, N.; Besson, M. Selective Aqueous Phase Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid over Pt/C Catalysts: Influence of the Base and Effect of Bismuth Promotion. *Green Chem.* **2013**, *15*, 2240−2251.

(796) Wang, Y.; Yu, K.; Lei, D.; Si, W.; Feng, Y.; Lou, L.-L.; Liu, S. Basicity-Tuned Hydrotalcite-Supported Pd Catalysts for Aerobic Oxidation of 5-Hydroxymethyl-2-Furfural under Mild Conditions. *ACS Sus. Chem. Eng.* **2016**, *4*, 4752−4761.

(797) Zhang, Z.; Zhen, J.; Liu, B.; Lv, K.; Deng, K. Selective Aerobic Oxidation of the Biomass-Derived Precursor 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid under Mild Conditions over a Magnetic Palladium Nanocatalyst. *Green Chem.* **2015**, *17*, 1308−1317.

(798) Cai, J.; Ma, H.; Zhang, J.; Song, Q.; Du, Z.; Huang, Y.; Xu, J. Gold Nanoclusters Confined in a Supercage of Y Zeolite for Aerobic Oxidation of Hmf under Mild Conditions. *Chem. Eur. J.* **2013**, *19*, 14215−14223.

(799) Miao, Z.; Zhang, Y.; Pan, X.; Wu, T.; Zhang, B.; Li, J.; Yi, T.; Zhang, Z.; Yang, X. Superior Catalytic Performance of Ce1-Xbixo2-Δ Solid Solution and Au/Ce1-Xbixo2-Δ for 5-Hydroxymethylfurfural Conversion in Alkaline Aqueous Solution. *Catal. Sci. Technol.* **2015**, *5*, 1314−1322.

(800) Gao, Z.; Xie, R.; Fan, G.; Yang, L.; Li, F. Highly Efficient and Stable Bimetallic Aupd over La-Doped Ca-Mg-Al Layered Double Hydroxide for Base-Free Aerobic Oxidation of 5-Hydroxymethylfurfural in Water. *ACS Sus. Chem. Eng.* **2017**, *5*, 5852−5861.

(801) Casanova, O.; Iborra, S.; Corma, A. Biomass into Chemicals: One Pot-Base Free Oxidative Esterification of 5-Hydroxymethyl-2-Furfural into 2,5-Dimethylfuroate with Gold on Nanoparticulated Ceria. *J. Catal.* **2009**, *265*, 109−116.

(802) Zheng, L.; Zhao, J.; Du, Z.; Zong, B.; Liu, H. Efficient Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid on Ru/C Catalysts. *Sci. China Chem.* **2017**, *60*, 950−957.

(803) Mishra, D. K.; Lee, H. J.; Kim, J.; Lee, H.-S.; Cho, J. K.; Suh, Y.-W.; Yi, Y.; Kim, Y. J. Mnco2o4 Spinel Supported Ruthenium Catalyst for Air-Oxidation of Hmf to Fdca under Aqueous Phase and Base-Free Conditions. *Green Chem.* **2017**, *19*, 1619−1623.

(804) Ventura, M.; Nocito, F.; de Giglio, E.; Cometa, S.; Altomare, A.; Dibenedetto, A. Tunable Mixed Oxides Based on Ceo2 for the Selective Aerobic Oxidation of 5-(Hydroxymethyl)Furfural to Fdca in Water. *Green Chem.* **2018**, *20*, 3921−3926.

(805) Gao, T.; Yin, Y.; Zhu, G.; Cao, Q.; Fang, W. Co3o4 Nps Decorated Mn-Co-O Solid Solution as Highly Selective Catalyst for Aerobic Base-Free Oxidation of 5-Hmf to 2,5-Fdca in Water. *Catal. Today* **2020**, *355*, 252−262.

(806) Neaţu, F.; Marin, R. S.; Florea, M.; Petrea, N.; Pavel, O. D.; Pârvulescu, V. I. Selective Oxidation of 5-Hydroxymethyl Furfural over Non-Precious Metal Heterogeneous Catalysts. *Appl. Catal. B: Environ.* **2016**, *180*, 751−757.

(807) Sun, K.-k.; Chen, S.-j.; Li, Z.-l.; Lu, G.-p.; Cai, C. Synthesis of a Zif-Derived Hollow Yolk-Shell Co@Cn Catalyst for the Oxidative Esterification of 5-Hydroxymethylfurfural. *Green Chem.* **2019**, *21*, 1602−1608.

(808) Nguyen, C. V.; Liao, Y.-T.; Kang, T.-C.; Chen, J. E.; Yoshikawa, T.; Nakasaka, Y.; Masuda, T.; Wu, K. C. W. A Metal-Free, High Nitrogen-Doped Nanoporous Graphitic Carbon Catalyst for an Effective Aerobic Hmf-to-Fdca Conversion. *Green Chem.* **2016**, *18*, 5957−5961.

(809) Rathod, P. V.; Jadhav, V. H. Efficient Method for Synthesis of 2,5-Furandicarboxylic Acid from 5-Hydroxymethylfurfural and Fructose Using Pd/Cc Catalyst under Aqueous Conditions. *ACS Sus. Chem. Eng.* **2018**, *6*, 5766−5771.

(810) Liu, H.; Cao, X.; Wang, T.; Wei, J.; Tang, X.; Zeng, X.; Sun, Y.; Lei, T.; Liu, S.; Lin, L. Efficient Synthesis of Bio-Monomer 2,5-

Furandicarboxylic Acid from Concentrated 5-Hydroxymethylfurfural or Fructose in Dmso/H2o Mixed Solvent. *J. Ind. Eng. Chem.* **2019**, *77*, 209−214.

(811) Motagamwala, A. H.; Won, W.; Sener, C.; Alonso, D. M.; Maravelias, C. T.; Dumesic, J. A. Toward Biomass-Derived Renewable Plastics: Production of 2,5-Furandicarboxylic Acid from Fructose. *Sci. Adv.* **2018**, *4*, No. eaap9722.

(812) Yi, G.; Teong, S. P.; Zhang, Y. The Direct Conversion of Sugars into 2,5-Furandicarboxylic Acid in a Triphasic System. *ChemSusChem* **2015**, *8*, 1151−1155.

(813) Corma, A.; Iborra, S.; Velty, A. Chemical Routes for the Transformation of Biomass into Chemicals. *Chem. Rev.* **2007**, *107*, 2411−2502.

(814) Soták, T.; Hronec, M.; Gál, M.; Dobročka, E.; Škriniarová, J. Aqueous-Phase Oxidation of Furfural to Maleic Acid Catalyzed by Copper Phosphate Catalysts. *Catal. Lett.* **2017**, *147*, 2714−2723.

(815) Chai, L.; Hou, X.; Cui, X.; Li, H.; Zhang, N.; Zhang, H.; Chen, C.; Wang, Y.; Deng, T. 5-Hydroxymethylfurfural Oxidation to Maleic Acid by O2 over Graphene Oxide Supported Vanadium: Solvent Effects and Reaction Mechanism. *Chem. Eng. J.* **2020**, *388*, 124187.

(816) Li, X.; Ko, J.; Zhang, Y. Highly Efficient Gas-Phase Oxidation of Renewable Furfural to Maleic Anhydride over Plate Vanadium Phosphorus Oxide Catalyst. *ChemSusChem* **2018**, *11*, 612−618.

(817) Mariscal, R.; Maireles-Torres, P.; Ojeda, M.; Sádaba, I.; López Granados, M. Furfural: A Renewable and Versatile Platform Molecule for the Synthesis of Chemicals and Fuels. *Energy & Environ. Sci.* **2016**, *9*, 1144−1189.

(818) Alonso-Fagúndez, N.; Ojeda, M.; Mariscal, R.; Fierro, J. L. G.; López Granados, M. Gas Phase Oxidation of Furfural to Maleic Anhydride on V2o5/Γ-Al2o3 Catalysts: Reaction Conditions to Slow Down the Deactivation. *J. Catal.* **2017**, *348*, 265−275.

(819) Shi, S.; Guo, H.; Yin, G. Synthesis of Maleic Acid from Renewable Resources: Catalytic Oxidation of Furfural in Liquid Media with Dioxygen. *Catal. Commun.* **2011**, *12*, 731−733.

(820) Choudhary, H.; Nishimura, S.; Ebitani, K. Highly Efficient Aqueous Oxidation of Furfural to Succinic Acid Using Reusable Heterogeneous Acid Catalyst with Hydrogen Peroxide. *Chem. Lett.* **2012**, *41*, 409−411.

(821) Rezaei, M.; Najafi Chermahini, A.; Dabbagh, H. A.; Saraji, M.; Shahvar, A. Furfural Oxidation to Maleic Acid with H2o2 by Using Vanadyl Pyrophosphate and Zirconium Pyrophosphate Supported on Well-Ordered Mesoporous Kit-6. *J. Environ. Chem. Eng.* **2019**, *7*, 102855.

(822) Alonso-Fagúndez, N.; Agirrezabal-Telleria, I.; Arias, P. L.; Fierro, J. L. G.; Mariscal, R.; Granados, M. L. Aqueous-Phase Catalytic Oxidation of Furfural with H2o2: High Yield of Maleic Acid by Using Titanium Silicalite-1. *RSC Adv.* **2014**, *4*, 54960−54972.

(823) Agirrezabal-Telleria, I.; Gandarias, I.; Arias, P. L. Production of Furfural from Pentosan-Rich Biomass: Analysis of Process Parameters During Simultaneous Furfural Stripping. *Bioresour. Technol.* **2013**, *143*, 258−264.

(824) Agirrezabal-Telleria, I.; Larreategui, A.; Requies, J.; Güemez, M. B.; Arias, P. L. Furfural Production from Xylose Using Sulfonic Ion-Exchange Resins (Amberlyst) and Simultaneous Stripping with Nitrogen. *Bioresour. Technol.* **2011**, *102*, 7478−7485.

(825) Milas, N. A.; Peeler, R. L.; Mageli, O. L. Organic Peroxides. Xix. A-Hydroperoxyethers and Related Peroxides. *J. American Chem. Soc.* **1954**, *76*, 2322−2325.

(826) Das, R. K.; Brar, S. K.; Verma, M. Enhanced Fumaric Acid Production from Brewery Wastewater by Immobilization Technique. *J. Chem. Technol. Biotechnol.* **2015**, *90*, 1473−1479.

(827) Li, Q.; Tao, W.; Li, A.; Zhou, Q.; Shuang, C. Poly (4-Vinylpyridine) Catalyzed Isomerization of Maleic Acid to Fumaric Acid. *Appl. Catal. A: General* **2014**, *484*, 148−153.

(828) Mittal, J.; Mathur, R. B.; Bahl, O. P.; Inagaki, M. Post Spinning Treatment of Pan Fibers Using Succinic Acid to Produce High Performance Carbon Fibers. *Carbon* **1998**, *36*, 893−897.

(829) Song, H.; Lee, S. Y. Production of Succinic Acid by Bacterial Fermentation. *Enzyme Microb. Technol.* **2006**, *39*, 352−361.

(830) Cheng, K.-K.; Zhao, X.-B.; Zeng, J.; Zhang, J.-A. Biotechnological Production of Succinic Acid: Current State and Perspectives. *Biofuels, Bioprod. & Bioref.* **2012**, *6*, 302−318.

(831) der Werf, M. J. V.; Guettler, M. V.; Jain, M. K.; Zeikus, J. G. Environmental and Physiological Factors Affecting the Succinate Product Ratio During Carbohydrate Fermentation by Actinobacillus Sp. 130z. *Arch. Microbiol.* **1997**, *167*, 332−342.

(832) Ghayur, A.; Verheyen, T. V.; Meuleman, E. Techno-Economic Analysis of a Succinic Acid Biorefinery Coproducing Acetic Acid and Dimethyl Ether. *J. Clean. Prod.* **2019**, *230*, 1165−1175.

(833) Li, C.; Ong, K. L.; Cui, Z.; Sang, Z.; Li, X.; Patria, R. D.; Qi, Q.; Fickers, P.; Yan, J.; Lin, C. S. K. Promising Advancement in Fermentative Succinic Acid Production by Yeast Hosts. *J. Hazard. Mater.* **2021**, *401*, 123414.

(834) Li, C.; Gao, S.; Yang, X.; Lin, C. S. K. Green and Sustainable Succinic Acid Production from Crude Glycerol by Engineered Yarrowia Lipolytica Via Agricultural Residue Based in Situ Fibrous Bed Bioreactor. *Bioresour. Technol.* **2018**, *249*, 612−619.

(835) Nghiem, N. P.; Kleff, S.; Schwegmann, S. Succinic Acid: Technology Development and Commercialization. *Fermentation (Basel)* **2017**, *3*, 26.

(836) Saxena, R. K.; Saran, S.; Isar, J.; Kaushik, R. 27 - Production and Applications Of succinic Acid. In *Current Developments in Biotechnology and Bioengineering*; Pandey, A., Negi, S., Soccol, C. R., Eds.; Elsevier, 2017; pp 601−630.

(837) Ong, K. L.; Li, C.; Li, X.; Zhang, Y.; Xu, J.; Lin, C. S. K. Co-Fermentation of Glucose and Xylose from Sugarcane Bagasse into Succinic Acid by Yarrowia Lipolytica. *Biochem. Eng. J.* **2019**, *148*, 108−115.

(838) Kamzolova, S. V.; Yusupova, A. I.; Vinokurova, N. G.; Fedotcheva, N. I.; Kondrashova, M. N.; Finogenova, T. V.; Morgunov, I. G. Chemically Assisted Microbial Production of Succinic Acid by the Yeast Yarrowia Lipolytica Grown on Ethanol. *Appl. Microbiol. & Biotechnol.* **2009**, *83*, 1027−1034.

(839) Kamzolova, S. V.; Vinokurova, N. G.; Yusupova, A. I.; Morgunov, I. G. Succinic Acid Production from N-Alkanes. *Eng. Life Sci.* **2012**, *12*, 560−566.

(840) Kamzolova, S. V.; Vinokurova, N. G.; Dedyukhina, E. G.; Samoilenko, V. A.; Lunina, J. N.; Mironov, A. A.; Allayarov, R. K.; Morgunov, I. G. The Peculiarities of Succinic Acid Production from Rapeseed Oil by Yarrowia Lipolytica Yeast. *Appl. Microbiol. & Biotechnol.* **2014**, *98*, 4149−4157.

(841) Dalli, S. S.; Tilaye, T. J.; Rakshit, S. K. Conversion of Wood-Based Hemicellulose Prehydrolysate into Succinic Acid Using a Heterogeneous Acid Catalyst in a Biphasic System. *Ind. Eng. Chem. Res.* **2017**, *56*, 10582−10590.

(842) Liu, Y.; Ma, C.; Huang, C.; Fu, Y.; Chang, J. Efficient Conversion of Xylose into Furfural Using Sulfonic Acid-Functionalized Metal-Organic Frameworks in a Biphasic System. *Ind. Eng. Chem. Res.* **2018**, *57*, 16628−16634.

(843) Choudhary, V.; Sandler, S. I.; Vlachos, D. G. Conversion of Xylose to Furfural Using Lewis and Brønsted Acid Catalysts in Aqueous Media. *ACS Catal.* **2012**, *2*, 2022−2028.

(844) Harmer, M. A.; Sun, Q. Solid Acid Catalysis Using Ion-Exchange Resins. *Appl. Catal. A: General* **2001**, *221*, 45−62.

(845) Thubsuang, U.; Chotirut, S.; Nuithitikul, K.; Payaka, A.; Manmuanpom, N.; Chaisuwan, T.; Wongkasemjit, S. Oxidative Upgrade of Furfural to Succinic Acid Using So3h-Carbocatalysts with Nitrogen Functionalities Based on Polybenzoxazine. *J. Colloid Interface Sci.* **2020**, *565*, 96−109.

(846) Pandey, S. K.; Yadav, S. P. S.; Prasad, M.; Prasad, J. Mechanism of Ru(III) Catalysis in Oxidation of Levulinic Acid by Acidic Solution of N-Bromobenzamide. *Asian J. Chem.* **1999**, *11*, 203−206.

(847) Van Es, D. S.; Van der Klis, F.; Van Haveren, J. Succinic Acid from Biomass. WO 2012/044168A1, 2012.

(848) Wee, S.-L.; Tye, C.-T.; Bhatia, S. Membrane Separation Process—Pervaporation through Zeolite Membrane. *Sep. Purif. Technol.* **2008**, *63*, 500−516.

(849) Chapman, P. D.; Oliveira, T.; Livingston, A. G.; Li, K. Membranes for the Dehydration of Solvents by Pervaporation. *J. Memb. Sci.* **2008**, *318*, 5−37.

(850) Deng, Y.; Mao, Y. Production of Adipic Acid by the Native-Occurring Pathway in Thermobifida Fusca B6. *J. Appl. Microbiol.* **2015**, *119*, 1057−1063.

(851) Zhao, M.; Huang, D. X.; Zhang, X. J.; Koffas, M. A. G.; Zhou, J. W.; Deng, Y. Metabolic Engineering of Escherichia Coli for Producing Adipic Acid through the Reverse Adipate-Degradation Pathway. *Metab. Eng.* **2018**, *47*, 254−262.

(852) Chae, T. U.; Choi, S. Y.; Ryu, J. Y.; Lee, S. Y. Production of Ethylene Glycol from Xylose by Metabolically Engineeredescherichia Coli. *AlChE J.* **2018**, *64*, 4193−4200.

(853) Pereira, B.; Li, Z.-J.; De Mey, M.; Lim, C. G.; Zhang, H.; Hoeltgen, C.; Stephanopoulos, G. Efficient Utilization of Pentoses for Bioproduction of the Renewable Two-Carbon Compounds Ethylene Glycol and Glycolate. *Metab. Eng.* **2016**, *34*, 80−87.

(854) Xin, B.; Tao, F.; Wang, Y.; Liu, H.; Ma, C.; Xu, P. Coordination of Metabolic Pathways: Enhanced Carbon Conservation in 1,3-Propanediol Production by Coupling with Optically Pure Lactate Biosynthesis. *Metab. Eng.* **2017**, *41*, 102−114.

(855) Celinska, E. Fully Glycerol-Independent Microbial Production of 1,3-Propanediol Via Non-Natural Pathway: Paving the Way to Success with Synthetic Tiles. *Biotechnol. J.* **2015**, *10*, 242−243.

(856) Tai, Y.-S.; Xiong, M.; Jambunathan, P.; Wang, J.; Wang, J.; Stapleton, C.; Zhang, K. Engineering Nonphosphorylative Metabolism to Generate Lignocellulose-Derived Products. *Nat. Chem. Biol.* **2016**, *12*, 247−253.

(857) Ma, C.; Wang, A.; Qin, J.; Li, L.; Ai, X.; Jiang, T.; Tang, H.; Xu, P. Enhanced 2,3-Butanediol Production by Klebsiella Pneumoniae Sdm. *Appl. Microbiol. & Biotechnol.* **2009**, *82*, 49−57.

(858) Liu, Y.; Cen, X.; Liu, D.; Chen, Z. Metabolic Engineering of Escherichia Coli for High-Yield Production of (R)-1,3-Butanediol. *ACS Synth. Biol.* **2021**, *10*, 1946−1955.

(859) Chae, T. U.; Kim, W. J.; Choi, S.; Park, S. J.; Lee, S. Y. Metabolic Engineering of Escherichia Coli for the Production of 1,3-Diaminopropane, a Three Carbon Diamine. *Sci. Rep.* **2015**, *5*, 13040.

(860) Noh, M.; Yoo, S. M.; Kim, W. J.; Lee, S. Y. Gene Expression Knockdown by Modulating Synthetic Small Rna Expression in Escherichia Coli. *Cell Syst.* **2017**, *5*, 418−426 e4.

(861) Ma, W.; Cao, W.; Zhang, H.; Chen, K.; Li, Y.; Ouyang, P. Enhanced Cadaverine Production from L-Lysine Using Recombinant Escherichia Coli Co-Overexpressing Cada and Cadb. *Biotechnol. Lett.* **2015**, *37*, 799−806.

(862) Kim, H. T.; Baritugo, K.-A.; Oh, Y. H.; Hyun, S. M.; Khang, T. U.; Kang, K. H.; Jung, S. H.; Song, B. K.; Park, K.; Kim, I.-K.; et al. Metabolic Engineering of Corynebacterium Glutamicum for the High-Level Production of Cadaverine That Can Be Used for the Synthesis of Biopolyamide 510. *ACS Sus. Chem. Eng.* **2018**, *6*, 5296−5305.

(863) Buschke, N.; Becker, J.; Schaefer, R.; Kiefer, P.; Biedendieck, R.; Wittmann, C. Systems Metabolic Engineering of Xylose-Utilizing Corynebacterium Glutamicum for Production of 1,5-Diaminopentane. *Biotechnol. J.* **2013**, *8*, 557−570.

(864) Podolean, I.; Rizescu, C.; Bala, C.; Rotariu, L.; Parvulescu, V. I.; Coman, S. M.; Garcia, H. Unprecedented Catalytic Wet Oxidation of Glucose to Succinic Acid Induced by the Addition of N-Butylamine to a Ruiii Catalyst. *ChemSusChem* **2016**, *9*, 2307−2311.

(865) Rios, J.; Lebeau, J.; Yang, T.; Li, S.; Lynch, M. D. A Critical Review on the Progress and Challenges to a More Sustainable, Cost Competitive Synthesis of Adipic Acid. *Green Chem.* **2021**, *23*, 3172−3190.

(866) Bart, J. C. J.; Cavallaro, S. Transiting from Adipic Acid to Bioadipic Acid. 1, Petroleum-Based Processes. *Ind. Eng. Chem. Res.* **2015**, *54*, 1−46.

(867) Agustriyanto, R.; Fatmawati, A. Model of Steady State Cyclohexane Oxidation for Ketone-Alcohol (K-a) Oil Production. *Makara J. Sci.* **2014**, *18*, 91−95.

(868) Takamatsu, Y.; Kaneshima, T. Process for the Preparation of Cyclohexanol. US 20030018223A1, 2003.

(869) EIA Administration. *Annual Energy Outlook 2021*; EIA Administration, 2021.

(870) U.S. EPA. *Inventory of Us Greenhouse Gas Emissions and Sinks*; U.S. EPA, 2017.

(871) Ehhalt, D.; Prather, M.; Dentener, F.; Derwent, R.; Dlugokencky, E. J.; Holland, E.; Isaksen, I.; Katima, J.; Kirchhoff, V.; Matson, P. et al. *Atmospheric Chemistry and Greenhouse Gases.*; Houghton, J. T., Ed.; Cambridge University Press: Cambridge, United Kingdom, 2001.

(872) Bart, J. C. J.; Cavallaro, S. Transiting from Adipic Acid to Bioadipic Acid. 1, Petroleum-Based Processes. *Ind. Eng. Chem. Res.* **2015**, *54*, 1−46.

(873) Schneider, L.; Lazarus, M.; Kollmus, A. *Industrial N2o Projects under the Cdm: Adipic Acid - a Case of Carbon Leakage?*; Stockholm Environment Institute, 2010.

(874) Shimizu, A.; Tanaka, K.; Fujimori, M. Abatement Technologies for N2o Emissions in the Adipic Acid Industry. *Chemosphere* **2000**, *2*, 425−434.

(875) Reimer, R. A.; Slaten, C. S.; Seapan, M. Abatement of N2o Emissions Produced in the Adipic Acid Industry. *Environ. Prog.* **1994**, *13*, 134−13.

(876) Van De Vyver, S.; Román-Leshkov, Y. Emerging Catalytic Processes for the Production of Adipic Acid. *Catal. Sci. Technol.* **2013**, *3*, 1465−1479.

(877) Lesage, G.; Quesada Peñate, I.; Cognet, P.; Poux, M. Green Process for Adipic Acid Synthesis: Oxidation by Hydrogen Peroxide in Water Micromelusions Using Benzalkonium Chloride C12-14 Surfactant. *Int. J. Chem. React. Eng.* **2012**, *10*, A47.

(878) Blach, P.; Böstrom, Z.; Franceschi-Messant, S.; Lattes, A.; Perez, E.; Rico-Lattes, I. Recyclable Process for Sustainable Adipic Acid Production in Microemulsions. *Tetra.* **2010**, *66*, 7124−7128.

(879) Jin, P.; Zhao, Z.; Dai, Z.; Wei, D.; Tang, M.; Wang, X. Influence of Reaction Conditions on Product Distribution in the Green Oxidation of Cyclohexene to Adipic Acid with Hydrogen Peroxide. *Catal. Today* **2011**, *175*, 619−624.

(880) Shang, M. *The Direct Synthesis of Adipic Acid from Cyclohexene and Hydrogen Peroxide by a Continuous Micro-Flow Process*; Eindhoven University of Technology, 2016.

(881) Usui, Y.; Sato, K. A Green Method of Adipic Acid Synthesis: Organic Solvent- and Halide-Free Oxidation of Cycloalkanones with 30% Hydrogen Peroxide. *Green Chem.* **2003**, *5*, 373−375.

(882) Sato, K.; Aoki, M.; Noyori, R. A ″Green″ Route to Adipic Acid: Direct Oxidation of Cyclohexenes with 30 Percent Hydrogen Peroxide. *Science* **1998**, *281*, 1646−7.

(883) Wen, Y.; Wang, X.; Wei, H.; Li, B.; Jin, P.; Li, L. A Large-Scale Continuous-Flow Process for the Production of Adipic Acid Via Catalytic Oxidation of Cyclohexene with H2o2. *Green Chem.* **2012**, *14*, 2868.

(884) Yan, W. J.; Zhang, W. X.; Xia, Q.; Wang, S. S.; Zhang, S. X.; Shen, J.; Jin, X. Highly Dispersed Metal Incorporated Hexagonal Mesoporous Silicates for Catalytic Cyclohexanone Oxidation to Adipic Acid. *Chin. J. Chem. Eng.* **2020**, *28*, 2542−2548.

(885) Wang, Q.; Vural Gürsel, I.; Shang, M.; Hessel, V. Life Cycle Assessment for the Direct Synthesis of Adipic Acid in Microreactors and Benchmarking to the Commercial Process. *Chem. Eng. J.* **2013**, *234*, 300−311.

(886) Castellan, A. Industrial Production and Use of Adipic Acid. *Catal. Today* **1991**, *9*, 237−254.

(887) Barker, R. S.; Cohen, M. A. Adipic Acid Production by the Two Step Oxidation of Cyclohexane with Oxygen. 3,234,271, 1966.

(888) Lidov, R. E. Process for Oxidising Cyclohexane to Adipic Acid. US 3361806, 1968.

(889) Skoog, E.; Shin, J. H.; Saez-Jimenez, V.; Mapelli, V.; Olsson, L. Biobased Adipic Acid - the Challenge of Developing the Production Host. *Biotechnol. Adv.* **2018**, *36*, 2248−2263.

(890) Von Kutepow, N. Production of Adipic Acid. US 3876695, 1975.

(891) Platz, R.; Kummer, R.; Schneider, H.-W.; Schwirten, K. Manufacture of Pent-3-Enoic Acid. US 4550195A, 1985.

(892) Cabrera Camacho, C. E.; Alonso-Fariñas, B.; Villanueva Perales, A. L.; Vidal-Barrero, F.; Ollero, P. Techno-Economic and Life-Cycle Assessment of One-Step Production of 1,3-Butadiene from Bioethanol Using Reaction Data under Industrial Operating Conditions. *ACS Sus. Chem. Eng.* **2020**, *8*, 10201−10211.

(893) Abdelrahman, O. A.; Park, D. S.; Vinter, K. P.; Spanjers, C. S.; Ren, L.; Cho, H. J.; Vlachos, D. G.; Fan, W.; Tsapatsis, M.; Dauenhauer, P. J. Biomass-Derived Butadiene by Dehydra-Decyclization of Tetrahydrofuran. *ACS Sus. Chem. Eng.* **2017**, *5*, 3732−3736.

(894) Polen, T.; Spelberg, M.; Bott, M. Toward Biotechnological Production of Adipic Acid and Precursors from Biorenewables. *J. Biotechnol.* **2013**, *167*, 75−84.

(895) Deng, Y.; Ma, L. Z.; Mao, Y. Biological Production of Adipic Acid from Renewable Substrates: Current and Future Methods. *Biochem. Eng. J.* **2016**, *105*, 16−26.

(896) Bart, J. C. J.; Cavallaro, S. Transiting from Adipic Acid to Bioadipic Acid. Part Ii. Biosynthetic Pathways. *Ind. Eng. Chem. Res.* **2015**, *54*, 567−576.

(897) Babu, T.; Yun, E. J.; Kim, S.; Kim, D. H.; Liu, K. H.; Kim, S. R.; Kim, K. H. Engineering Escherichia Coli for the Production of Adipic Acid through the Reversed Β-Oxidation Pathway. *Proc. Biochem.* **2015**, *50*, 2066−2071.

(898) Burgard, A. P.; Pharkya, P.; Osterhout, R. E. Microorganisms for the Production of Adipic Acid and Other Compounds. US 7,799,545 B2, 2010.

(899) Yu, J.-L.; Xia, X.-X.; Zhong, J.-J.; Qian, Z.-G. Direct Biosynthesis of Adipic Acid from a Synthetic Pathway in Recombinantescherichia Coli. *Biotechnol. Bioeng.* **2014**, *111*, 2580−2586.

(900) Zhao, M.; Huang, D.; Zhang, X.; Koffas, M. A. G.; Zhou, J.; Deng, Y. Metabolic Engineering of Escherichia Coli for Producing Adipic Acid through the Reverse Adipate-Degradation Pathway. *Metab. Eng.* **2018**, *47*, 254−262.

(901) Clomburg, J. M.; Blankschien, M. D.; Vick, J. E.; Chou, A.; Kim, S.; Gonzalez, R. Integrated Engineering of Β-Oxidation Reversal and Ω-Oxidation Pathways for the Synthesis of Medium Chain Ω-Functionalized Carboxylic Acids. *Metab. Eng.* **2015**, *28*, 202−212.

(902) Kruyer, N. S.; Peralta-Yahya, P. Metabolic Engineering Strategies to Bio-Adipic Acid Production. *Curr. Opin. Biotechnol.* **2017**, *45*, 136−143.

(903) Picataggio, S.; Beardslee, T. Biological Methods for Preparing Adipic Acid. US 2012/0021474 A1, 2012.

(904) Picataggio, S.; Deanda, K.; Mielenz, J. Determination of Candida Tropicalis Acyl Coenzyme a Oxidase Isozyme Function by Sequential Gene Disruption. *Mol. Cell. Biol.* **1991**, *11*, 4333−4339.

(905) McCoy, M. Verdezyne Advances Biobased Adipic Acid. https://cen.acs.org/articles/89/i49/Verdezyne-Advances-Biobased-Adipic-Acid.html (accessed 20/01/2022).

(906) Winters, P. Advancing the Biobased Economy: Renewable Chemical Biorefinery Commercialization, Progress, and Market Opportunities, 2016 and Beyond. *Ind. Biotechnol.* **2016**, *12*, 290−294.

(907) Guzman, D. d. Verzedyne Exit Confirmed. https://greenchemicalsblog.com/2018/05/24/verdezyne-exit-confirmed/ (accessed 20/01/2022).

(908) Turk, S. C. H. J.; Kloosterman, W. P.; Ninaber, D. K.; Kolen, K. P. A. M.; Knutova, J.; Suir, E.; Schürmann, M.; Raemakers-Franken, P. C.; Müller, M.; De Wildeman, S. M. A.; et al. Metabolic Engineering toward Sustainable Production of Nylon-6. *ACS Synth. Biol.* **2016**, *5*, 65−73.

(909) Deng, Y.; Ma, L.; Mao, Y. Biological Production of Adipic Acid from Renewable Substrates: Current and Future Methods. *Biochem. Eng. J.* **2016**, *105*, 16−26.

(910) Moon, T. S.; Yoon, S. H.; Lanza, A. M.; Roy-Mayhew, J. D.; Prather, K. L. Production of Glucaric Acid from a Synthetic Pathway in Recombinant Escherichia Coli. *Appl. Environ. Microbiol* **2009**, *75*, 589−95.

(911) Johnson, C. W.; Salvachua, D.; Khanna, P.; Smith, H.; Peterson, D. J.; Beckham, G. T. Enhancing Muconic Acid Production from Glucose and Lignin-Derived Aromatic Compounds Via Increased Protocatechuate Decarboxylase Activity. *Metab. Eng. Commun.* **2016**, *3*, 111−119.

(912) Mizuno, S.; Yoshikawa, N.; Seki, M.; Mikawa, T.; Imada, Y. Microbial Production of Cis, Cis-Muconic Acid from Benzoic Acid. *Appl. Microbiol. Biotechnol.* **1988**, *28*, 20−25.

(913) Xie, N.-Z.; Liang, H.; Huang, R.-B.; Xu, P. Biotechnological Production of Muconic Acid: Current Status and Future Prospects. *Biotechnol. Adv.* **2014**, *32*, 615−622.

(914) Zółtaszek, R.; Hanausek, M.; Kilińska, Z. a. M.; Walaszek, Z. The Biological Role of D-Glucaric Acid and Its Derivatives: Potential Use in Medicine. *Postepy Hig. Med. Dosw.* **2008**, *62*, 451−462.

(915) Paulik, F. E.; Hershman, A.; Knox, W. R.; Roth, J. F. Production of Dicarboxylic Acids. US 4060547, 1977.

(916) Yim, H.; Haselbeck, R.; Niu, W.; Pujol-Baxley, C.; Burgard, A.; Boldt, J.; Khandurina, J.; Trawick, J. D.; Osterhout, R. E.; Stephen, R.; et al. Metabolic Engineering of Escherichia Coli for Direct Production of 1,4-Butanediol. *Nat. Chem. Biol.* **2011**, *7*, 445−452.

(917) Walaszek, Z. Potential Use of D-Glucaric Acid Derivatives in Cancer Prevention. *Cancer Lett.* **1990**, *54*, 1−8.

(918) Moon, T. S.; Dueber, J. E.; Shiue, E.; Prather, K. L. J. Use of Modular, Synthetic Scaffolds for Improved Production of Glucaric Acid in Engineered E. Coli. *Metab. Eng.* **2010**, *12*, 298−305.

(919) Shiue, E.; Prather, K. L. J. Improving D-Glucaric Acid Production from Myo-Inositol in E. Coli by Increasing Miox Stability and Myo-Inositol Transport. *Metab. Eng.* **2014**, *22*, 22−31.

(920) Chen, N.; Wang, J.; Zhao, Y.; Deng, Y. Metabolic Engineering of Saccharomyces Cerevisiae for Efficient Production of Glucaric Acid at High Titer. *Microb. Cell Fact.* **2018**, *17*, 67.

(921) Gupta, A.; Hicks, M. A.; Manchester, S. P.; Prather, K. L. J. Porting the Synthetic D-Glucaric Acid Pathway from Escherichia Coli to Saccharomyces Cerevisiae. *Biotechnol. J.* **2016**, *11*, 1201−1208.

(922) Liu, Y.; Gong, X.; Wang, C.; Du, G.; Chen, J.; Kang, Z. Production of Glucaric Acid from Myo-Inositol in Engineered Pichia Pastoris. *Enzyme Microb. Technol.* **2016**, *91*, 8−16.

(923) Diamond, G. M.; Murphy, V.; Boussie, T. R. Application of High Throughput Experimentation to the Production of Commodity Chemicals from Renewable Feedstocks. In *Modern Applications of High Throughput R&D in Heterogeneous Catalysis*; Bentham Books, 2014.

(924) Lange, J. P. Renewable Feedstocks: The Problem of Catalyst Deactivation and Its Mitigation. *Angew. Chem., Int. Ed.* **2015**, *54*, 13186−97.

(925) Jin, X.; Liu, M. Y.; Zhang, G. Y.; Wang, J. Y.; Xia, Q.; Sun, Y.; Zhou, Z. Q.; Zhang, W. X.; Wang, S.; Lam, C. H.; et al. Chemical Synthesis of Adipic Acid from Glucose and Derivatives: Challenges for Nanocatalyst Design. *ACS Sus. Chem. Eng.* **2020**, *8*, 18732−18754.

(926) Niu, W.; Draths, K. M.; Frost, J. W. Benzene-Free Synthesis of Adipic Acid. *Biotechnol. Prog.* **2002**, *18*, 201−211.

(927) Averesch, N. J. H.; Kromer, J. O. Metabolic Engineering of the Shikimate Pathway for Production of Aromatics and Derived Compounds-Present and Future Strain Construction Strategies. *Front. Bioeng. Biotechnol.* **2018**, *6*, 1−19.

(928) Jung, H. M.; Jung, M. Y.; Oh, M. K. Metabolic Engineering of Klebsiella Pneumoniae for the Production of Cis,Cis-Muconic Acid. *Appl. Microbiol. Biotechnol.* **2015**, *99*, 5217−25.

(929) Bui, V.; Lau, M. K.; MacRae, D.; Schnweitzer, D. Methods for Producing Isomers of Muconic Acid. US 8,809,583 B2, 2014.

(930) Averesch, N. J. H.; Krömer, J. O. Tailoring Strain Construction Strategies for Muconic Acid Production in S. Cerevisiae and E. Coli. *Metab. Eng. Commun.* **2014**, *1*, 19−28.

(931) Curran, K. A.; Leavitt, J. M.; Karim, A. S.; Alper, H. S. Metabolic Engineering of Muconic Acid Production in Saccharomyces Cerevisiae. *Metab. Eng.* **2013**, *15*, 55−66.

(932) Khalil, I.; Quintens, G.; Junkers, T.; Dusselier, M. Muconic Acid Isomers as Platform Chemicals and Monomers in the Biobased Economy. *Green Chem.* **2020**, *22*, 1517−1541.

(933) Salvachua, D.; Johnson, C. W.; Singer, C. A.; Rohrer, H.; Peterson, D. J.; Black, B. A.; Knapp, A.; Beckham, G. T. Bioprocess Development for Muconic Acid Production from Aromatic Compounds and Lignin. *Green Chem.* **2018**, *20*, 5007−5019.

(934) Jastrzebski, R.; Van Den Berg, E. J.; Weckhuysen, B. M.; Bruijnincx, P. C. A. Sustainable Production of Dimethyl Adipate by Non-Heme Iron(Iii) Catalysed Oxidative Cleavage of Catechol. *Catal. Sci. Technol.* **2015**, *5*, 2103−2109.

(935) Coupe, F.; Petitjean, L.; Anastas, P. T.; Caijo, F.; Escande, V.; Darcel, C. Sustainable Oxidative Cleavage of Catechols for the Synthesis of Muconic Acid and Muconolactones Including Lignin Upgrading. *Green Chem.* **2020**, *22*, 6204−6211.

(936) Raj, K.; Partow, S.; Correia, K.; Khusnutdinova, A. N.; Yakunin, A. F.; Mahadevan, R. Biocatalytic Production of Adipic Acid from Glucose Using Engineered Saccharomyces Cerevisiae. *Metab. Eng. Commun.* **2018**, *6*, 28−32.

(937) Joo, J. C.; Khusnutdinova, A. N.; Flick, R.; Kim, T.; Bornscheuer, U. T.; Yakunin, A. F.; Mahadevan, R. Alkene Hydrogenation Activity of Enoate Reductases for an Environmentally Benign Biosynthesis of Adipic Acid. *Chem. Sci.* **2017**, *8*, 1406−1413.

(938) López-Garzón, C. S.; Straathof, A. J. J. Recovery of Carboxylic Acids Produced by Fermentation. *Biotechnol. Adv.* **2014**, *32*, 873−904.

(939) Djas, M.; Henczka, M. Reactive Extraction of Carboxylic Acids Using Organic Solvents and Supercritical Fluids: A Review. *Sep. Purif. Technol.* **2018**, *201*, 106−119.

(940) Datta, D.; Kumar, S.; Uslu, H. Status of the Reactive Extraction as a Method of Separation. *J. Chem.* **2015**, *2015*, 1−16.

(941) Van Osch, D. J. G. P.; Dietz, C. H. J. T.; Van Spronsen, J.; Kroon, M. C.; Gallucci, F.; Van Sint Annaland, M.; Tuinier, R. A Search for Natural Hydrophobic Deep Eutectic Solvents Based on Natural Components. *ACS Sus. Chem. Eng.* **2019**, *7*, 2933−2942.

(942) Zia, F.; Zia, K. M.; Zuber, M.; Kamal, S.; Aslam, N. Starch Based Polyurethanes: A Critical Review Updating Recent Literature. *Carbohydr. Polym.* **2015**, *134*, 784−98.

(943) Johnson, C. W.; Salvachúa, D.; Rorrer, N. A.; Black, B. A.; Vardon, D. R.; St. John, P. C.; Cleveland, N. S.; Dominick, G.; Elmore, J. R.; Grundl, N.; et al. Innovative Chemicals and Materials from Bacterial Aromatic Catabolic Pathways. *Joule* **2019**, *3*, 1523−1537.

(944) Ludmila, H.; Michel, J.; Andrea, S.; Ales, H. Lignin-Potential Products and Their Market Value. *Wood Res.* **2015**, *60*, 973−986.

(945) Kamlet, J. Process for the Manufacture of Pimelic Acid. US 2826609, 1958.

(946) Long, D. J. G. Production of Pimelic Acid. US 2800507, 1957.

(947) Hawkins, E. G. E.; Stern, E. S. Manufacture of Pimelic Acid and Intermediates Therefor. US 2698339, 1954.

(948) Zhang, W.-W.; Yang, M.-M.; Li, H.-x.; Wang, D. Construction of Recombinant Bacillus Subtilis Strains for Efficient Pimelic Acid Synthesis. *Electron. J. Biotechnol.* **2011**, *14*, 1−1.

(949) Wang, F.; Zhao, J.; Li, Q.; Yang, J.; Li, R.; Min, J.; Yu, X.; Zheng, G.-W.; Yu, H.-L.; Zhai, C.; et al. One-Pot Biocatalytic Route from Cycloalkanes to A,Ω-Dicarboxylic Acids by Designed Escherichia Coli Consortia. *Nat. Commun.* **2020**, *11*, 5035.

(950) Molitor, E. J.; Mullen, B. D. Method of Manufacture of Octanedioic Acid, Precursors, and Derivatives. US 20160031790A1, 2016.

(951) Goebel, C. G.; Brown, A. C.; Oehlschlaeger, H. F.; Rolfes, R. P. Method of Making Azelaic Acid. US 2813113, 1957.

(952) Noyori, R.; Aoki, M.; Sato, K. Green Oxidation with Aqueous Hydrogen Peroxide. *Chem. Commun.* **2003**, 1977−1986.

(953) Köckritz, A.; Martin, A. Synthesis of Azelaic Acid from Vegetable Oil-Based Feedstocks. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 83−91.

(954) Oakley, M. A.; Woodward, S.; Coupland, K.; Parker, D.; Temple-Heald, C. Practical Dihydroxylation and C-C Cleavage of Unsaturated Fatty Acids. *J. Mol. Catal. A: Chem.* **1999**, *150*, 105−111.

(955) Köckritz, A.; Blumenstein, M.; Martin, A. Catalytic Cleavage of Methyl Oleate or Oleic Acid. *Eur. J. Lipid Sci. Technol.* **2010**, *112*, 58−63.

(956) Godard, A.; De Caro, P.; Thiebaud-Roux, S.; Vedrenne, E.; Mouloungui, Z. New Environmentally Friendly Oxidative Scission of Oleic Acid into Azelaic Acid and Pelargonic Acid. *J. American Oil Chem. Soc.* **2013**, *90*, 133−140.

(957) Benessere, V.; Cucciolito, M. E.; De Santis, A.; Di Serio, M.; Esposito, R.; Ruffo, F.; Turco, R. Sustainable Process for Production of Azelaic Acid through Oxidative Cleavage of Oleic Acid. *J. American Oil Chem. Soc.* **2015**, *92*, 1701−1707.

(958) Vasishtha, A. K.; Trivedi, R. K.; Das, G. Sebacic Acid and 2-Octanol from Castor Oil. *J. American Oil Chem. Soc.* **1990**, *67*, 333−337.

(959) Li, G.; Huang, D.; Sui, X.; Li, S.; Huang, B.; Zhang, X.; Wu, H.; Deng, Y. Advances in Microbial Production of Medium-Chain Dicarboxylic Acids for Nylon Materials. *React. Chem. Eng.* **2020**, *5*, 221−238.

(960) Song, J.-W.; Jeon, E.-Y.; Song, D.-H.; Jang, H.-Y.; Bornscheuer, U. T.; Oh, D.-K.; Park, J.-B. Multistep Enzymatic Synthesis of Long-Chain A,Ω-Dicarboxylic and Ω-Hydroxycarboxylic Acids from Renewable Fatty Acids and Plant Oils. *Angew. Chem., Int. Ed.* **2013**, *52*, 2534−2537.

(961) Sugiharto, Y. E. C.; Lee, H.; Fitriana, A. D.; Lee, H.; Jeon, W.; Park, K.; Ahn, J.; Lee, H. Effect of Decanoic Acid and 10-Hydroxydecanoic Acid on the Biotransformation of Methyl Decanoate to Sebacic Acid. *AMB Express* **2018**, *8*, 75.

(962) Sarria, S.; Kruyer, N. S.; Peralta-Yahya, P. Microbial Synthesis of Medium-Chain Chemicals from Renewables. *Nat. Biotechnol.* **2017**, *35*, 1158−1166.

(963) Choi, Y. J.; Lee, S. Y. Microbial Production of Short-Chain Alkanes. *Nature* **2013**, *502*, 571−574.

(964) Beardslee, T.; Picataggio, S.; Eiruch, L. D.; Laplaza, J. M. Biological Methods for Preparing a Fatty Dicaboxylic Acid. US 9938544B2, 2018.

(965) Lee, H.; Sugiharto, Y. E. C.; Lee, H.; Jeon, W.; Ahn, J.; Lee, H. Biotransformation of Dicarboxylic Acids from Vegetable Oil-Derived Sources: Current Methods and Suggestions for Improvement. *Appl. Microbiol. Biotechnol.* **2019**, *103*, 1545−1555.

(966) Ngo, H. L.; Jones, K.; Foglia, T. A. Metathesis of Unsaturated Fatty Acids: Synthesis of Long-Chain Unsaturated-A,Ω-Dicarboxylic Acids. *J. Am. Oil Chem. Soc.* **2006**, *83*, 629−634.

(967) Croda Pripol Dimer Acids and Dimer Diols. https://www.crodasmartmaterials.com/en-gb/brands/pripol (accessed 22/03/2022).

(968) Hwang, K. C.; Sagadevan, A.; Kundu, P. The Sustainable Room Temperature Conversion of P-Xylene to Terephthalic Acid Using Ozone and Uv Irradiation. *Green Chem.* **2019**, *21*, 6082−6088.

(969) Lin, Y.-C.; Huber, G. W. The Critical Role of Heterogeneous Catalysis in Lignocellulosic Biomass Conversion. *Energy & Environ. Sci.* **2009**, *2*, 68−80.

(970) Carlson, T. R.; Cheng, Y.-T.; Jae, J.; Huber, G. W. Production of Green Aromatics and Olefins by Catalytic Fast Pyrolysis of Wood Sawdust. *Energy & Environ. Sci.* **2011**, *4*, 145−161.

(971) Cheng, Y.-T.; Jae, J.; Shi, J.; Fan, W.; Huber, G. W. Production of Renewable Aromatic Compounds by Catalytic Fast Pyrolysis of Lignocellulosic Biomass with Bifunctional Ga/Zsm-5 Catalysts. *Angew. Chem., Int. Ed.* **2012**, *51*, 1387−1390.

(972) Cheng, Y.-T.; Huber, G. W. Production of Targeted Aromatics by Using Diels-Alder Classes of Reactions with Furans and Olefins over Zsm-5. *Green Chem.* **2012**, *14*, 3114−3125.

(973) Cheng, Y.-T.; Wang, Z.; Gilbert, C. J.; Fan, W.; Huber, G. W. Production of P-Xylene from Biomass by Catalytic Fast Pyrolysis Using Zsm-5 Catalysts with Reduced Pore Openings. *Angew. Chem., Int. Ed.* **2012**, *51*, 11097−11100.

(974) Minty, J. J.; Singer, M. E.; Scholz, S. A.; Bae, C.-H.; Ahn, J.-H.; Foster, C. E.; Liao, J. C.; Lin, X. N. Design and Characterization of Synthetic Fungal-Bacterial Consortia for Direct Production of Isobutanol from Cellulosic Biomass. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 14592−14597.

(975) Lin, Z.; Nikolakis, V.; Ierapetritou, M. Alternative Approaches for P-Xylene Production from Starch: Techno-Economic Analysis. *Ind. Eng. Chem. Res.* **2014**, *53*, 10688−10699.

(976) Román-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. Production of Dimethylfuran for Liquid Fuels from Biomass-Derived Carbohydrates. *Nature* **2007**, *447*, 982−985.

(977) Zhao, R.; Zhao, Z.; Li, S.; Parvulescu, A.-N.; Müller, U.; Zhang, W. Excellent Performances of Dealuminated H-Beta Zeolites from Organotemplate-Free Synthesis in Conversion of Biomass-Derived 2,5-Dimethylfuran to Renewable P-Xylene. *ChemSusChem* **2018**, *11*, 3803−3811.

(978) Nikbin, N.; Do, P. T.; Caratzoulas, S.; Lobo, R. F.; Dauenhauer, P. J.; Vlachos, D. G. A Dft Study of the Acid-Catalyzed Conversion of 2,5-Dimethylfuran and Ethylene to P-Xylene. *J. Catal.* **2013**, *297*, 35−43.

(979) Nikbin, N.; Feng, S.; Caratzoulas, S.; Vlachos, D. G. P-Xylene Formation by Dehydrative Aromatization of a Diels-Alder Product in Lewis and Brønsted Acidic Zeolites. *J. Phys. Chem. C* **2014**, *118*, 24415−24424.

(980) Li, Y.-P.; Head-Gordon, M.; Bell, A. T. Computational Study of P-Xylene Synthesis from Ethylene and 2,5-Dimethylfuran Catalyzed by H-Bea. *J. Phys. Chem. C* **2014**, *118*, 22090−22095.

(981) Kim, T.-W.; Kim, S.-Y.; Kim, J.-C.; Kim, Y.; Ryoo, R.; Kim, C.-U. Selective P-Xylene Production from Biomass-Derived Dimethylfuran and Ethylene over Zeolite Beta Nanosponge Catalysts. *Appl. Catal. B: Environ.* **2016**, *185*, 100−109.

(982) Zhao, R.; Xu, L.; Huang, S.; Zhang, W. Highly Selective Production of Renewable P-Xylene from Bio-Based 2,5-Dimethylfuran and Ethylene over Al-Modified H-Beta Zeolites. *Catal. Sci. Technol.* **2019**, *9*, 5676−5685.

(983) Williams, C. L.; Chang, C.-C.; Do, P.; Nikbin, N.; Caratzoulas, S.; Vlachos, D. G.; Lobo, R. F.; Fan, W.; Dauenhauer, P. J. Cycloaddition of Biomass-Derived Furans for Catalytic Production of Renewable P-Xylene. *ACS Catal.* **2012**, *2*, 935−939.

(984) Chen, Z.; Liao, S.; Ge, L.; Amaniampong, P. N.; Min, Y.; Wang, C.; Li, K.; Lee, J.-M. Reduced Graphene Oxide with Controllably Intimate Bifunctionality for the Catalytic Transformation of Fructose into 2,5-Diformylfuran in Biphasic Solvent Systems. *Chem. Eng. J.* **2020**, *379*, 122284.

(985) Kania, J.; Blommel, P.; Woods, E.; Dally, B.; Lyman, W.; Cortright, R. Production of Distillate Fuels from Biomass-Dervied Polyoxygenates. US 2013/0263498A1, 2013.

(986) Norris, S. *Virent Bioformpx Paraxylene Used to Produce World's First 100% Plant Based Polyester Shirts*; Virent, Inc., 2016.

(987) Norris, S. *Virent Bioformpx Paraxylene Used for World's First Pet Plastic Bottle Made Entirely from Plant-Based Material*; Virent, Inc., 2015.

(988) Behling, R.; Valange, S.; Chatel, G. Heterogeneous Catalytic Oxidation for Lignin Valorization into Valuable Chemicals: What Results? What Limitations? What Trends? *Green Chem.* **2016**, *18*, 1839−1854.

(989) Roberts, V. M.; Stein, V.; Reiner, T.; Lemonidou, A.; Li, X.; Lercher, J. A. Towards Quantitative Catalytic Lignin Depolymerization. *Chem. Eur. J.* **2011**, *17*, 5939−5948.

(990) Mota, M. I. F.; Rodrigues Pinto, P. C.; Loureiro, J. M.; Rodrigues, A. E. Recovery of Vanillin and Syringaldehyde from Lignin Oxidation: A Review of Separation and Purification Processes. *Sep. Purif. Rev.* **2016**, *45*, 227−259.

(991) Sun, Z.; Fridrich, B.; de Santi, A.; Elangovan, S.; Barta, K. Bright Side of Lignin Depolymerization: Toward New Platform Chemicals. *Chem. Rev.* **2018**, *118*, 614−678.

(992) Shuai, L.; Amiri, M. T.; Questell-Santiago, Y. M.; Heroguel, F.; Li, Y.; Kim, H.; Meilan, R.; Chapple, C.; Ralph, J.; Luterbacher, J. S. Formaldehyde Stabilization Facilitates Lignin Monomer Production During Biomass Depolymerization. *Science* **2016**, *354*, 329−333.

(993) Yan, N.; Zhao, C.; Dyson, P. J.; Wang, C.; Liu, L.-t.; Kou, Y. Selective Degradation of Wood Lignin over Noble-Metal Catalysts in a Two-Step Process. *ChemSusChem* **2008**, *1*, 626−629.

(994) Chen, S.; Wojcieszak, R.; Dumeignil, F.; Marceau, E.; Royer, S. How Catalysts and Experimental Conditions Determine the Selective Hydroconversion of Furfural and 5-Hydroxymethylfurfural. *Chem. Rev.* **2018**, *118*, 11023−11117.

(995) Gandini, A.; Silvestre, A. J. D.; Neto, C. P.; Sousa, A. F.; Gomes, M. The Furan Counterpart of Poly(Ethylene Terephthalate): An Alternative Material Based on Renewable Resources. *J. Polym. Sci. A: Polym. Chem.* **2009**, *47*, 295−298.

(996) Avantium Avantium Yxy Technology. https://www.avantium.com/technologies/yxy/ (accessed 22/03/2022).

(997) Yi, G.; Teong, S. P.; Li, X.; Zhang, Y. Purification of Biomass-Derived 5-Hydroxymethylfurfural and Its Catalytic Conversion to 2,5-Furandicarboxylic Acid. *ChemSusChem* **2014**, *7*, 2131−2135.

(998) Yi, G.; Teong, S. P.; Zhang, Y. Base-Free Conversion of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid over a Ru/C Catalyst. *Green Chem.* **2016**, *18*, 979−983.

(999) Yu, H.; Wu, Z.; Wei, Z.; Zhai, Y.; Ru, S.; Zhao, Q.; Wang, J.; Han, S.; Wei, Y. N-Formylation of Amines Using Methanol as a Potential Formyl Carrier by a Reusable Chromium Catalyst. *Commun. Chem.* **2019**, *2*, 15.

(1000) Chen, C.-T.; Nguyen, C. V.; Wang, Z.-Y.; Bando, Y.; Yamauchi, Y.; Bazziz, M. T. S.; Fatehmulla, A.; Farooq, W. A.; Yoshikawa, T.; Masuda, T.; et al. Hydrogen Peroxide Assisted Selective Oxidation of 5-Hydroxymethylfurfural in Water under Mild Conditions. *ChemCatChem.* **2018**, *10*, 361−365.

(1001) Zhao, D.; Rodriguez-Padron, D.; Triantafyllidis, K. S.; Wang, Y.; Luque, R.; Len, C. Microwave-Assisted Oxidation of Hydroxymethyl Furfural to Added-Value Compounds over a Ruthenium-Based Catalyst. *ACS Sus. Chem. Eng.* **2020**, *8*, 3091−3102.

(1002) Wang, S.; Zhang, Z.; Liu, B. Catalytic Conversion of Fructose and 5-Hydroxymethylfurfural into 2,5-Furandicarboxylic Acid over a Recyclable Fe3o4-Coox Magnetite Nanocatalyst. *ACS Sus. Chem. Eng.* **2015**, *3*, 406−412.

(1003) Yan, D.; Wang, G.; Gao, K.; Lu, X.; Xin, J.; Zhang, S. One-Pot Synthesis of 2,5-Furandicarboxylic Acid from Fructose in Ionic Liquids. *Ind. Eng. Chem. Res.* **2018**, *57*, 1851−1858.

(1004) Islam, M. A.; Hadadi, N.; Ataman, M.; Hatzimanikatis, V.; Stephanopoulos, G. Exploring Biochemical Pathways for Mono-Ethylene Glycol (Meg) Synthesis from Synthesis Gas. *Metab. Eng.* **2017**, *41*, 173−181.

(1005) Zhang, M.; Yu, Y. Dehydration of Ethanol to Ethylene. *Ind. Eng. Chem. Res.* **2013**, *52*, 9505−9514.

(1006) Dever, J. P.; George, K. F.; Hoffman, W. C.; Soo, H. Ethylene Oxide. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley-VCH, 2000.

(1007) Li, Y.; Yue, B.; Yan, S.; Yang, W.; Xie, Z.; Chen, Q.; He, H. Preparation of Ethylene Glycol Via Catalytic Hydration with Highly Efficient Supported Niobia Catalyst. *Catal. Lett.* **2004**, *95*, 163−166.

(1008) Tuck, C. O.; Perez, E.; Horvath, I. T.; Sheldon, R. A.; Poliakoff, M. Valorization of Biomass: Deriving More Value from Waste. *Science* **2012**, *337*, 695−699.

(1009) Rebsdat, S.; Mayer, D. Ethylene Glycol. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Elvers, B., Ed.; Wiley-VCH Verlag GmbH & Co.: Hoboken, NJ, 2000; Vol. *13*, pp 288−292.

(1010) Ruppert, A. M.; Weinberg, K.; Palkovits, R. Hydrogenolysis Goes Bio: From Carbohydrates and Sugar Alcohols to Platform Chemicals. *Angew. Chem., Int. Ed.* **2012**, *51*, 2564−2601.

(1011) Marchesan, A. N.; Oncken, M. P.; Maciel Filho, R.; Wolf Maciel, M. R. A Roadmap for Renewable C2-C3 Glycols Production: A Process Engineering Approach. *Green Chem.* **2019**, *21*, 5168−5194.

(1012) Ji, N.; Zhang, T.; Zheng, M.; Wang, A.; Wang, H.; Wang, X.; Chen, J. G. Direct Catalytic Conversion of Cellulose into Ethylene Glycol Using Nickel-Promoted Tungsten Carbide Catalysts. *Angew. Chem., Int. Ed.* **2008**, *47*, 8510−8513.

(1013) Zheng, M.; Pang, J.; Wang, A.; Zhang, T. One-Pot Catalytic Conversion of Cellulose to Ethylene Glycol and Other Chemicals: From Fundamental Discovery to Potential Commercialization. *Chin. J. Catal.* **2014**, *35*, 602−613.

(1014) Zheng, M.; Pang, J.; Sun, R.; Wang, A.; Zhang, T. Selectivity Control for Cellulose to Diols: Dancing on Eggs. *ACS Catal.* **2017**, *7*, 1939−1954.

(1015) Xu, G.; Wang, A.; Pang, J.; Zheng, M.; Yin, J.; Zhang, T. Remarkable Effect of Extremely Dilute H2so4 on the Cellulose Conversion to Ethylene Glycol. *Appl. Catal. A: General* **2015**, *502*, 65−70.

(1016) Wang, A.; Zhang, T. One-Pot Conversion of Cellulose to Ethylene Glycol with Multifunctional Tungsten-Based Catalysts. *Acc. Chem. Res.* **2013**, *46*, 1377−1386.

(1017) Zhao, G.; Zheng, M.; Sun, R.; Tai, Z.; Pang, J.; Wang, A.; Wang, X.; Zhang, T. Ethylene Glycol Production from Glucose over W-Ru Catalysts: Maximizing Yield by Kinetic Modeling and Simulation. *AlChE J.* **2017**, *63*, 2072−2080.

(1018) Pan, G.-Y.; Ma, Y.-L.; Ma, X.-X.; Sun, Y.-G.; Lv, J.-M.; Zhang, J.-L. Catalytic Hydrogenation of Corn Stalk into Polyol over Ni-W/Mcm-41 Catalyst. *Chem. Eng. J.* **2016**, *299*, 386−392.

(1019) Yang, H.; Wei, W.; Wu, S.; Zhuang, J. Effective Conversion of Acid Pretreated Pulp to Ethylene Glycol over Ordered Mesoporous Wo3 Catalyst. *Ind. Crops Prod.* **2018**, *124*, 863−869.

(1020) te Molder, T. D. J.; Kersten, S. R. A.; Lange, J. P.; Ruiz, M. P. Ethylene Glycol from Lignocellulosic Biomass: Impact of Lignin on Catalytic Hydrogenolysis. *Ind. Eng. Chem. Res.* **2021**, *60*, 7043−7049.

(1021) Pang, J.; Zheng, M.; Wang, A.; Zhang, T. Catalytic Hydrogenation of Corn Stalk to Ethylene Glycol and 1,2-Propylene Glycol. *Ind. Eng. Chem. Res.* **2011**, *50*, 6601−6608.

(1022) Pang, J.; Zheng, M.; Wang, A.; Sun, R.; Wang, H.; Jiang, Y.; Zhang, T. Catalytic Conversion of Concentrated Miscanthus in Water for Ethylene Glycol Production. *AlChE J.* **2014**, *60*, 2254−2262.

(1023) Ooms, R.; Dusselier, M.; Geboers, J. A.; Op De Beeck, B.; Verhaeven, R.; Gobechiya, E.; Martens, J. A.; Redl, A.; Sels, B. F. Conversion of Sugars to Ethylene Glycol with Nickel Tungsten Carbide in a Fed-Batch Reactor: High Productivity and Reaction Network Elucidation. *Green Chem.* **2014**, *16*, 695−707.

(1024) Zhao, G.; Zheng, M.; Zhang, J.; Wang, A.; Zhang, T. Catalytic Conversion of Concentrated Glucose to Ethylene Glycol with Semicontinuous Reaction System. *Ind. Eng. Chem. Res.* **2013**, *52*, 9566−9572.

(1025) Fang, Z.-H.; Zhang, J.; Lu, Q.-M.; Bao, J. Process Development of Short-Chain Polyols Synthesis from Corn Stover by Combination of Enzymatic Hydrolysis and Catalytic Hydrogenolysis. *Biotechnol. Rep.* **2014**, *3*, 15−20.

(1026) Pang, J.; Zheng, M.; Li, X.; Jiang, Y.; Zhao, Y.; Wang, A.; Wang, J.; Wang, X.; Zhang, T. Selective Conversion of Concentrated Glucose to 1,2-Propylene Glycol and Ethylene Glycol by Using Rusn/Ac Catalysts. *Appl. Catal. B: Environ.* **2018**, *239*, 300−308.

(1027) Chu, D.; Zhao, C. Reduced Oxygen-Deficient Cuwo4 with Ni Catalyzed Selective Hydrogenolysis of Cellulose to Ethylene Glycol. *Catal. Today* **2020**, *351*, 125−132.

(1028) Feng, Y.; Yin, H.; Wang, A.; Shen, L.; Yu, L.; Jiang, T. Gas Phase Hydrogenolysis of Glycerol Catalyzed by Cu/Zno/Mox (Mox=Al2o3, Tio2, and Zro2) Catalysts. *Chem. Eng. J.* **2011**, *168*, 403−412.

(1029) Jiang, T.; Zhou, Y.; Liang, S.; Liu, H.; Han, B. Hydrogenolysis of Glycerol Catalyzed by Ru-Cu Bimetallic Catalysts Supported on Clay with the Aid of Ionic Liquids. *Green Chem.* **2009**, *11*, 1000−1006.

(1030) Dhale, A. D.; Myrant, L. K.; Chopade, S. P.; Jackson, J. E.; Miller, D. J. Propylene Glycol and Ethylene Glycol Recovery from Aqueous Solution Via Reactive Distillation. *Chem. Eng. Sci.* **2004**, *59*, 2881−2890.

(1031) Sun, D.; Yamada, Y.; Sato, S. Effect of Ag Loading on Cu/Al2o3 Catalyst in the Production of 1,2-Propanediol from Glycerol. *Appl. Catal. A: General* **2014**, *475*, 63−68.

(1032) Avantium Plantmeg. https://www.avantium.com/lead-products/#plantmeg (accessed 21/03/2022).

(1033) Van Der Waal, J. C. Process for Preparing Ethylene Glycol from a Carbohydrate Source. US 20170362146A1, 2017.

(1034) Wojcik, A. *Braskem and Haldor Topsoe Achieve First Production of Bio-Based Meg from Sugar*; Topsoe, 2020.

(1035) Majerski, P. A.; Piskorz, J. K. R.; Desmond St, A. G. Hadlein Production of Glycolaldehyde by Hydrous Thermolysis of Sugars. US 7094932, 2006.

(1036) Osmundsen, C. M.; Taarning, E.; Holm, M. S. Process for the Preparation of Ethylene Glycol from Sugars. US 9926247, 2018.

(1037) Sasaki, M.; Goto, K.; Tajima, K.; Adschiri, T.; Arai, K. Rapid and Selective Retro-Aldol Condensation of Glucose to Glycolaldehyde in Supercritical Water. *Green Chem.* **2002**, *4*, 285−287.

(1038) Zhang, Y.; Liu, D.; Chen, Z. Production of C2-C4 Diols from Renewable Bioresources: New Metabolic Pathways and Metabolic Engineering Strategies. *Biotechnol. Biofuels* **2017**, *10*, 299.

(1039) Devadas, V. V.; Khoo, K. S.; Chia, W. Y.; Chew, K. W.; Munawaroh, H. S. H.; Lam, M. K.; Lim, J. W.; Ho, Y. C.; Lee, K. T.; Show, P. L. Algae Biopolymer Towards Sustainable Circular Economy. *Bioresour. Technol.* **2021**, *325*, 124702.

(1040) Dugar, D.; Stephanopoulos, G. Relative Potential of Biosynthetic Pathways for Biofuels and Bio-Based Products. *Nat. Biotechnol.* **2011**, *29*, 1074−1078.

(1041) Chen, Z.; Huang, J.; Wu, Y.; Liu, D. Metabolic Engineering of Corynebacterium Glutamicum for the De Novo Production of Ethylene Glycol from Glucose. *Metab. Eng.* **2016**, *33*, 12−18.

(1042) Pereira, B.; Zhang, H.; De Mey, M.; Lim, C. G.; Li, Z.-J.; Stephanopoulos, G. Engineering a Novel Biosynthetic Pathway in Escherichia Coli for Production of Renewable Ethylene Glycol. *Biotechnol. Bioeng.* **2016**, *113*, 376−383.

(1043) Li, K.; Sun, W.; Meng, W.; Yan, J.; Zhang, Y.; Guo, S.; Lü, C.; Ma, C.; Gao, C. Production of Ethylene Glycol from Glycerol Using an in Vitro Enzymatic Cascade. *Catalysts* **2021**, *11*, 214.

(1044) Hamdy, M. S.; Eissa, M. A.; Keshk, S. M. A. S. New Catalyst with Multiple Active Sites for Selective Hydrogenolysis of Cellulose to Ethylene Glycol. *Green Chem.* **2017**, *19*, 5144−5151.

(1045) Zheng, M.-Y.; Wang, A.-Q.; Ji, N.; Pang, J.-F.; Wang, X.-D.; Zhang, T. Transition Metal-Tungsten Bimetallic Catalysts for the Conversion of Cellulose into Ethylene Glycol. *ChemSusChem* **2010**, *3*, 63−66.

(1046) Li, N.; Zheng, Y.; Wei, L.; Teng, H.; Zhou, J. Metal Nanoparticles Supported on Wo3 Nanosheets for Highly Selective Hydrogenolysis of Cellulose to Ethylene Glycol. *Green Chem.* **2017**, *19*, 682−691.

(1047) Xiao, Z.; Jin, S.; Sha, G.; Williams, C. T.; Liang, C. Two-Step Conversion of Biomass-Derived Glucose with High Concentration over Cu-Cr Catalysts. *Ind. Eng. Chem. Res.* **2014**, *53*, 8735−8743.

(1048) Xiao, Z.; Jin, S.; Pang, M.; Liang, C. Conversion of Highly Concentrated Cellulose to 1,2-Propanediol and Ethylene Glycol over Highly Efficient Cucr Catalysts. *Green Chem.* **2013**, *15*, 891−895.

(1049) Zhou, L.; Wang, A.; Li, C.; Zheng, M.; Zhang, T. Selective Production of 1,2-Propylene Glycol from Jerusalem Artichoke Tuber Using Ni-W2c/Ac Catalysts. *ChemSusChem* **2012**, *5*, 932−938.

(1050) Arundhathi, R.; Mizugaki, T.; Mitsudome, T.; Jitsukawa, K.; Kaneda, K. Highly Selective Hydrogenolysis of Glycerol to 1,3-Propanediol over a Boehmite-Supported Platinum/Tungsten Catalyst. *ChemSusChem* **2013**, *6*, 1345−1347.

(1051) Priya, S. S.; Bhanuchander, P.; Kumar, V. P.; Bhargava, S. K.; Chary, K. V. R. Activity and Selectivity of Platinum-Copper Bimetallic Catalysts Supported on Mordenite for Glycerol Hydrogenolysis to 1,3-Propanediol. *Ind. Eng. Chem. Res.* **2016**, *55*, 4461−4472.

(1052) Chen, L.-F.; Guo, P.-J.; Zhu, L.-J.; Qiao, M.-H.; Shen, W.; Xu, H.-L.; Fan, K.-N. Preparation of Cu/Sba-15 Catalysts by Different Methods for the Hydrogenolysis of Dimethyl Maleate to 1,4-Butanediol. *Appl. Catal. A: General* **2009**, *356*, 129−136.

(1053) Minh, D. P.; Besson, M.; Pinel, C.; Fuertes, P.; Petitjean, C. Aqueous-Phase Hydrogenation of Biomass-Based Succinic Acid to 1,4-Butanediol over Supported Bimetallic Catalysts. *Top. Catal.* **2010**, *53*, 1270−1273.

(1054) Li, F.; Lu, T.; Chen, B.; Huang, Z.; Yuan, G. Pt Nanoparticles over Tio2-Zro2Mixed Oxide as Multifunctional

Catalysts for an Integrated Conversion of Furfural to 1,4-Butanediol. *Appl. Catal. A: General* **2014**, *478*, 252−258.

(1055) He, J.; Huang, K.; Barnett, K. J.; Krishna, S. H.; Alonso, D. M.; Brentzel, Z. J.; Burt, S. P.; Walker, T.; Banholzer, W. F.; Maravelias, C. T.; et al. New Catalytic Strategies for Alpha,Omega-Diols Production from Lignocellulosic Biomass. *Faraday Discuss.* **2017**, *202*, 247−267.

(1056) Xiao, B.; Zheng, M.; Li, X.; Pang, J.; Sun, R.; Wang, H.; Pang, X.; Wang, A.; Wang, X.; Zhang, T. Synthesis of 1,6-Hexanediol from Hmf over Double-Layered Catalysts of Pd/Sio2 + Ir-Reox/Sio2 in a Fixed-Bed Reactor. *Green Chem.* **2016**, *18*, 2175−2184.

(1057) Allgeier, A. M.; De Silva, W. I. N.; Korovessi, E.; Menning, C. A.; Ritter, J. C.; Sengupta, S. K.; Stauffer, C. S. Process for Preparing 1,6-Hexanediol. US 8962894 B2, 2015.

(1058) Gonzalez-Garay, A.; Gonzalez-Miquel, M.; Guillen-Gosalbez, G. High-Value Propylene Glycol from Low-Value Biodiesel Glycerol: A Techno-Economic and Environmental Assessment under Uncertainty. *ACS Sus. Chem. Eng.* **2017**, *5*, 5723−5732.

(1059) Company, A. D. M. Life Cycle Analysis of Bio-Propylene Glycol. https://www.adm.com/products-services/industrials/propylene-glycol/life-cycle-analysis (accessed 24/03/2022).

(1060) Oleon Minister-President Kris Peeters Starts up Oleon's New Bio-Propylene Glycol Unit. https://www.oleon.com/news/minister-president-kris-peeters-starts-up-oleon%E2%80%99s-new-bio-propylene-glycol-unit (accessed 24/03/2022).

(1061) Akiyama, M.; Sato, S.; Takahashi, R.; Inui, K.; Yokota, M. Dehydration-Hydrogenation of Glycerol into 1,2-Propanediol at Ambient Hydrogen Pressure. *Appl. Catal. A: General* **2009**, *371*, 60−66.

(1062) Suppes, G. J. Method of Producing Lower Alcohols from Glycerol. US 8252961, 2012.

(1063) Schüth, F. Chapter 1 - Hydrogen: Economics and Its Role in Biorefining. In *Catalytic Hydrogenation for Biomass Valorization*; The Royal Society of Chemistry, 2015; pp 1−21.

(1064) Liu, C.; Zhang, C.; Hao, S.; Sun, S.; Liu, K.; Xu, J.; Zhu, Y.; Li, Y. Wox Modified Cu/Al2o3 as a High-Performance Catalyst for the Hydrogenolysis of Glucose to 1,2-Propanediol. *Catal. Today* **2016**, *261*, 116−127.

(1065) Liu, C.; Zhang, C.; Sun, S.; Liu, K.; Hao, S.; Xu, J.; Zhu, Y.; Li, Y. Effect of Wox on Bifunctional Pd-Wox/Al2o3 Catalysts for the Selective Hydrogenolysis of Glucose to 1,2-Propanediol. *ACS Catal.* **2015**, *5*, 4612−4623.

(1066) Cameron, D. C.; Cooney, C. L. A Novel Fermentation - the Production of R(−)-1,2-Propanediol and Acetol by Clostridium-Thermosaccharolyticum. *Bio-technol.* **1986**, *4*, 651−654.

(1067) Clomburg, J. M.; Gonzalez, R. Metabolic Engineering of Escherichia Coli for the Production of 1,2-Propanediol from Glycerol. *Biotechnol. Bioeng.* **2011**, *108*, 867−879.

(1068) Jung, J.-Y.; Yun, H. S.; Lee, J.; Oh, M.-K. Production of 1,2-Propanediol from Glycerol in Saccharomyces Cerevisiae. *J. Microbiol. Biotechnol.* **2011**, *21*, 846−853.

(1069) Li, H.; Liao, J. C. Engineering a Cyanobacterium as the Catalyst for the Photosynthetic Conversion of Co2 to 1,2-Propanediol. *Microb. Cell Fact.* **2013**, *12*, 4.

(1070) Jain, R.; Sun, X.; Yuan, Q.; Yan, Y. Systematically Engineering Escherichia Coil for Enhanced Production of 1,2-Propanediol and 1-Propanol. *ACS Synth. Biol.* **2015**, *4*, 746−756.

(1071) Jain, R.; Huang, J.; Yuan, Q.; Yan, Y. Engineering Microaerobic Metabolism of E-Coli for 1,2-Propanediol Production. *J. Ind. Microbiol. Biotechnol.* **2015**, *42*, 1049−1055.

(1072) Conrado, R. J.; Wu, G. C.; Boock, J. T.; Xu, H.; Chen, S. Y.; Lebar, T.; Turnsek, J.; Tomsic, N.; Avbelj, M.; Gaber, R.; et al. DNA-Guided Assembly of Biosynthetic Pathways Promotes Improved Catalytic Efficiency. *Nucleic Acids Res.* **2012**, *40*, 1879−1889.

(1073) Lee, M. J.; Brown, I. R.; Juodeikis, R.; Frank, S.; Warren, M. J. Employing Bacterial Microcompartment Technology to Engineer a Shell-Free Enzyme-Aggregate for Enhanced 1,2-Propanediol Production in Escherichia Coli. *Metab. Eng.* **2016**, *36*, 48−56.

(1074) Niu, W.; Guo, J. Stereospecific Microbial Conversion of Lactic Acid into 1,2-Propanediol. *ACS Synth. Biol.* **2015**, *4*, 378−382.

(1075) Lee, C. S.; Aroua, M. K.; Daud, W. M. A. W.; Cognet, P.; Peres-Lucchese, Y.; Fabre, P.-L.; Reynes, O.; Latapie, L. A review: Conversion of bioglycerol into 1,3-propanediol via biological and chemical method. *Renew. Sus. Energy Rev.* **2015**, *42*, 963−972.

(1076) Tee, Z. K.; Jahim, J. M.; Tan, J. P.; Kim, B. H. Preeminent Productivity of 1,3-Propanediol by Clostridium Butyricum Jkt37 and the Role of Using Calcium Carbonate as Ph Neutraliser in Glycerol Fermentation. *Bioresour. Technol.* **2017**, *233*, 296−304.

(1077) Feng, S.; Zhao, B.; Liu, L.; Dong, J. Platinum Supported on Wo3-Doped Aluminosilicate: A Highly Efficient Catalyst for Selective Hydrogenolysis of Glycerol to 1,3-Propanediol. *Ind. Eng. Chem. Res.* **2017**, *56*, 11065−11074.

(1078) Zhu, S.; Zhu, Y.; Hao, S.; Chen, L.; Zhang, B.; Li, Y. Aqueous-Phase Hydrogenolysis of Glycerol to 1,3-Propanediol over Pt-H4siw12o40/Sio2. *Catal. Lett.* **2012**, *142*, 267−274.

(1079) Posada, J. A.; Rincón, L. E.; Cardona, C. A. Design and Analysis of Biorefineries Based on Raw Glycerol: Addressing the Glycerol Problem. *Bioresour. Technol.* **2012**, *111*, 282−293.

(1080) Vaidyanathan, H.; Kandasamy, V.; Ramakrishnan, G. G.; Ramachandran, K. B.; Jayaraman, G.; Ramalingam, S. Glycerol Conversion to 1, 3-Propanediol Is Enhanced by the Expression of a Heterologous Alcohol Dehydrogenase Gene in Lactobacillus Reuteri. *AMB Express* **2011**, *1*, 37.

(1081) Maervoet, V. E. T.; De Maeseneire, S. L.; Avci, F. G.; Beauprez, J.; Soetaert, W. K.; De Mey, M. High Yield 1,3-Propanediol Production by Rational Engineering of the 3-Hydroxypropionaldehyde Bottleneck in Citrobacter Werkmanii. *Microb. Cell Fact.* **2016**, *15*, 23.

(1082) Gonzalez-Pajuelo, M.; Meynial-Salles, I.; Mendes, F.; Andrade, J. C.; Vasconcelos, I.; Soucaille, P. Metabolic Engineering of Clostridium Acetobutylicum for the Industrial Production of 1,3-Propanediol from Glycerol. *Metab. Eng.* **2005**, *7*, 329−336.

(1083) Wang, W.; Sun, J. B.; Hartlep, M.; Deckwer, W. D.; Zeng, A. P. Combined Use of Proteomic Analysis and Enzyme Activity Assays for Metabolic Pathway Analysis of Glycerol Fermentation by Klebsiella Pneumoniae. *Biotechnol. Bioeng.* **2003**, *83*, 525−536.

(1084) Saxena, R. K.; Anand, P.; Saran, S.; Isar, J. Microbial Production of 1,3-Propanediol: Recent Developments and Emerging Opportunities. *Biotechnol. Adv.* **2009**, *27*, 895−913.

(1085) Zeng, A.-P.; Sabra, W. Microbial Production of Diols as Platform Chemicals: Recent Progresses. *Curr. Opin. Biotechnol.* **2011**, *22*, 749−757.

(1086) Chen, Z.; Liu, D. Toward Glycerol Biorefinery: Metabolic Engineering for the Production of Biofuels and Chemicals from Glycerol. *Biotechnol. Biofuels* **2016**, *9*, 205.

(1087) Xu, Y.-Z.; Guo, N.-N.; Zheng, Z.-M.; Ou, X.-J.; Liu, H.-J.; Liu, D.-H. Metabolism in 1,3-Propanediol Fed-Batch Fermentation by a D-Lactate Deficient Mutant of Klebsiella Pneumoniae. *Biotechnol. Bioeng.* **2009**, *104*, 965−972.

(1088) Zhang, Y.; Li, Y.; Du, C.; Liu, M.; Cao, Z. a. Inactivation of Aldehyde Dehydrogenase: A Key Factor for Engineering 1,3-Propanediol Production by Klebsiella Pneumoniae. *Metab. Eng.* **2006**, *8*, 578−586.

(1089) Seo, M.-Y.; Seo, J.-W.; Heo, S.-Y.; Baek, J.-O.; Rairakhwada, D.; Oh, B.-R.; Seo, P.-S.; Choi, M. H.; Kim, C. H. Elimination of by-Product Formation During Production of 1,3-Propanediol in Klebsiella Pneumoniae by Inactivation of Glycerol Oxidative Pathway. *Appl. Microbiol. & Biotechnol.* **2009**, *84*, 527−534.

(1090) Ko, Y.; Seol, E.; Sekar, B. S.; Kwon, S.; Lee, J.; Park, S. Metabolic Engineering of Klebsiella Pneumoniae J2b for Co-Production of 3-Hydroxypropionic Acid and 1,3-Propanediol from Glycerol: Reduction of Acetate and Other by-Products. *Bioresour. Technol.* **2017**, *244*, 1096−1103.

(1091) Huang, J.; Wu, Y.; Wu, W.; Zhang, Y.; Liu, D.; Chen, Z. Cofactor Recycling for Co-Production of 1,3-Propanediol and Glutamate by Metabolically Engineered Corynebacterium Glutamicum. *Sci. Rep.* **2017**, *7*, 42246.

(1092) Nakamura, C. E.; Whited, G. M. Metabolic Engineering for the Microbial Production of 1,3-Propanediol. *Curr. Opin. Biotechnol.* **2003**, *14*, 454−459.

(1093) Chen, Z.; Geng, F.; Zeng, A.-P. Protein Design and Engineering of a De Novo Pathway for Microbial Production of 1,3-Propanediol from Glucose. *Biotechnol. J.* **2015**, *10*, 284−289.

(1094) Chen, Z.; Rappert, S.; Zeng, A.-P. Rational Design of Allosteric Regulation of Homoserine Dehydrogenase by a Nonnatural Inhibitor L-Lysine. *ACS Synth. Biol.* **2015**, *4*, 126−131.

(1095) Chen, L.; Chen, Z.; Zheng, P.; Sun, J.; Zeng, A.-P. Study and Reengineering of the Binding Sites and Allosteric Regulation of Biosynthetic Threonine Deaminase by Isoleucine and Valine in Escherichia Coli. *Appl. Microbiol. & Biotechnol.* **2013**, *97*, 2939−2949.

(1096) Lee, K. H.; Park, J. H.; Kim, T. Y.; Kim, H. U.; Lee, S. Y. Systems Metabolic Engineering of Escherichia Coli for L-Threonine Production. *Mol. Sys. Biol.* **2007**, *3*, 149.

(1097) Szmidt-Middleton, H. L.; Ouellet, M.; Adams, P. D.; Keasling, J. D.; Mukhopadhyay, A. Utilizing a Highly Responsive Gene, Yhjx, in E. Coli Based Production of 1,4-Butanediol. *Chem. Eng. Sci.* **2013**, *103*, 68−73.

(1098) Chen, Z.; Wu, Y.; Huang, J.; Liu, D. Metabolic Engineering of Klebsiella Pneumoniae for the De Novo Production of 2-Butanol as a Potential Biofuel. *Bioresour. Technol.* **2015**, *197*, 260−265.

(1099) Chen, Z.; Sun, H.; Huang, J.; Wu, Y.; Liu, D. Metabolic Engineering of Klebsiella Pneumoniae for the Production of 2-Butanone from Glucose. *PLoS One* **2015**, *10*, No. e0140508.

(1100) Duan, H.; Yamada, Y.; Sato, S. Efficient Production of 1,3-Butadiene in the Catalytic Dehydration of 2,3-Butanediol. *Appl. Catal. A: General* **2015**, *491*, 163−169.

(1101) Kataoka, N.; Vangnai, A. S.; Ueda, H.; Tajima, T.; Nakashimada, Y.; Kato, J. Enhancement of (R)-1,3-Butanediol Production by Engineered Escherichia Coli Using a Bioreactor System with Strict Regulation of Overall Oxygen Transfer Coefficient and Ph. *Biosci. Biotechnol. Biochem.* **2014**, *78*, 695−700.

(1102) Huang, Z.; Barnett, K. J.; Chada, J. P.; Brentzel, Z. J.; Xu, Z.; Dumesic, J. A.; Huber, G. W. Hydrogenation of Γ-Butyrolactone to 1,4-Butanediol over Cuco/Tio2 Bimetallic Catalysts. *ACS Catal.* **2017**, *7*, 8429−8440.

(1103) Ding, G.; Zhu, Y.; Zheng, H.; Zhang, W.; Li, Y. Study on the Reaction Pathway in the Vapor-Phase Hydrogenation of Biomass-Derived Diethyl Succinate over Cuo/Zno Catalyst. *Catal. Commun.* **2010**, *11*, 1120−1124.

(1104) Sun, D.; Sato, S.; Ueda, W.; Primo, A.; Garcia, H.; Corma, A. Production of C4 and C5 Alcohols from Biomass-Derived Materials. *Green Chem.* **2016**, *18*, 2579−2597.

(1105) Besson, M.; Gallezot, P.; Pinel, C. Conversion of Biomass into Chemicals over Metal Catalysts. *Chem. Rev.* **2014**, *114*, 1827−1870.

(1106) Liu, X.; Wang, X.; Xu, G.; Liu, Q.; Mu, X.; Liu, H. Tuning the Catalytic Selectivity in Biomass-Derived Succinic Acid Hydrogenation on Feox-Modified Pd Catalysts. *J. Mater. Chem. A* **2015**, *3*, 23560−23569.

(1107) Li, X.; Jia, P.; Wang, T. Furfural: A Promising Platform Compound for Sustainable Production of C4 and C5 Chemicals. *ACS Catal.* **2016**, *6*, 7621−7640.

(1108) Luque, R.; Clark, J. H.; Yoshida, K.; Gai, P. L. Efficient Aqueous Hydrogenation of Biomass Platform Molecules Using Supported Metal Nanoparticles on Starbons®. *Chem. Commun.* **2009**, 5305−5307.

(1109) Corbel-Demailly, L.; Ly, B.-K.; Minh, D.-P.; Tapin, B.; Especel, C.; Epron, F.; Cabiac, A.; Guillon, E.; Besson, M.; Pinel, C. Heterogeneous Catalytic Hydrogenation of Biobased Levulinic and Succinic Acids in Aqueous Solutions. *ChemSusChem* **2013**, *6*, 2388−2395.

(1110) Li, X.; Lan, X.; Wang, T. Highly Selective Catalytic Conversion of Furfural to Γ-Butyrolactone. *Green Chem.* **2016**, *18*, 638−642.

(1111) Li, X.; Ho, B.; Zhang, Y. Selective Aerobic Oxidation of Furfural to Maleic Anhydride with Heterogeneous Mo-V-O Catalysts. *Green Chem.* **2016**, *18*, 2976−2980.

(1112) De Bari, I.; Giuliano, A.; Petrone, M. T.; Stoppiello, G.; Fatta, V.; Giardi, C.; Razza, F.; Novelli, A. From Cardoon Lignocellulosic Biomass to Bio-1,4 Butanediol: An Integrated Biorefinery Model. *Processes* **2020**, *8*, 1585.

(1113) Kim, B.; Lee, S.; Park, J.; Lu, M.; Oh, M.; Kim, Y.; Lee, J. Enhanced 2,3-Butanediol Production in Recombinant Klebsiella Pneumoniae Via Overexpression of Synthesis-Related Genes. *J. Microbiol. Biotechnol.* **2012**, *22*, 1258−1263.

(1114) Jung, M.-Y.; Mazumdar, S.; Shin, S. H.; Yang, K.-S.; Lee, J.; Oh, M.-K. Improvement of 2,3-Butanediol Yield in Klebsiella Pneumoniae by Deletion of the Pyruvate Formate-Lyase Gene. *Appl. Environ. Microbiol.* **2014**, *80*, 6195−6203.

(1115) Wang, Y.; Li, L.; Ma, C.; Gao, C.; Tao, F.; Xu, P. Engineering of Cofactor Regeneration Enhances (2s,3s)-2,3-Butanediol Production from Diacetyl. *Sci. Rep.* **2013**, *3*, 2643.

(1116) Yang, T.; Rao, Z.; Zhang, X.; Xu, M.; Xu, Z.; Yang, S.-T. Enhanced 2,3-Butanediol Production from Biodiesel-Derived Glycerol by Engineering of Cofactor Regeneration and Manipulating Carbon Flux in Bacillus Amyloliquefaciens. *Microb.. Cell Fact.* **2015**, *14*, 122.

(1117) Li, L.; Li, K.; Wang, Y.; Chen, C.; Xu, Y.; Zhang, L.; Han, B.; Gao, C.; Tao, F.; Ma, C.; et al. Metabolic Engineering of Enterobacter Cloacae for High-Yield Production of Enantiopure (2r,3r)-2,3-Butanediol from Lignocellulose-Derived Sugars. *Metab. Eng.* **2015**, *28*, 19−27.

(1118) Guo, X.; Cao, C.; Wang, Y.; Li, C.; Wu, M.; Chen, Y.; Zhang, C.; Pei, H.; Xiao, D. Effect of the Inactivation of Lactate Dehydrogenase, Ethanol Dehydrogenase, and Phosphotransacetylase on 2,3-Butanediol Production in Klebsiella Pneumoniae Strain. *Biotechnol. Biofuels* **2014**, *7*, 44.

(1119) Lian, J.; Chao, R.; Zhao, H. Metabolic Engineering of a Saccharomyces Cerevisiae Strain Capable of Simultaneously Utilizing Glucose and Galactose to Produce Enantiopure (2r,3r)-Butanediol. *Metab. Eng.* **2014**, *23*, 92−99.

(1120) Park, J. M.; Rathnasingh, C.; Song, H. Metabolic Engineering of Klebsiella Pneumoniae Based on in Silico Analysis and Its Pilot-Scale Application for 1,3-Propanediol and 2,3-Butanediol Co-Production. *J. Ind. Microbiol. Biotechnol.* **2017**, *44*, 431−441.

(1121) Andreozzi, S.; Chakrabarti, A.; Soh, K. C.; Burgard, A.; Yang, T. H.; Van Dien, S.; Miskovic, L.; Hatzimanikatis, V. Identification of Metabolic Engineering Targets for the Enhancement of 1,4-Butanediol Production in Recombinant E. Coli Using Large-Scale Kinetic Models. *Metab. Eng.* **2016**, *35*, 148−159.

(1122) Kataoka, N.; Vangnai, A. S.; Tajima, T.; Nakashimada, Y.; Kato, J. Improvement of (R)-1,3-Butanediol Production by Engineered Escherichia Coli. *J. Biosci. Bioeng.* **2013**, *115*, 475−480.

(1123) Werle, P.; Morawietz, M.; Lundmark, S.; Sörensen, K.; Karvinen, E.; Lehtonen, J. Alcohols, Polyhydric. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH, 2008; pp 263−281.

(1124) Scarlett, J.; Wood, M. A.; Willett, P. Process for the Recovery of Pentane-1,5-Diol. EP 104863 B1, 2003.

(1125) Schwarz, W.; Schossig, J.; Rossbacher, R.; Höke, H. Butyrolactone. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH, 2000; pp 69−83.

(1126) Sitthisa, S.; Sooknoi, T.; Ma, Y.; Balbuena, P. B.; Resasco, D. E. Kinetics and Mechanism of Hydrogenation of Furfural on Cu/Sio2 Catalysts. *J. Catal.* **2011**, *277*, 1−13.

(1127) Nakagawa, Y.; Nakazawa, H.; Watanabe, H.; Tomishige, K. Total Hydrogenation of Furfural over a Silica-Supported Nickel Catalyst Prepared by the Reduction of a Nickel Nitrate Precursor. *ChemCatChem.* **2012**, *4*, 1791−1797.

(1128) Sulmonetti, T. P.; Pang, S. H.; Claure, M. T.; Lee, S.; Cullen, D. A.; Agrawal, P. K.; Jones, C. W. Vapor Phase Hydrogenation of Furfural over Nickel Mixed Metal Oxide Catalysts Derived from Layered Double Hydroxides. *Appl. Catal. A: General* **2016**, *517*, 187−195.

(1129) Buntara, T.; Noel, S.; Phua, P. H.; Melián-Cabrera, I.; De Vries, J. G.; Heeres, H. J. Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone. *Angew. Chem., Int. Ed.* **2011**, *50*, 7083−7087.

(1130) Buntara, T.; Noel, S.; Phua, P. H.; Melián-Cabrera, I.; de Vries, J. G.; Heeres, H. J. From 5-Hydroxymethylfurfural (Hmf) to Polymer Precursors: Catalyst Screening Studies on the Conversion of 1,2,6-Hexanetriol to 1,6-Hexanediol. *Top. Catal.* **2012**, *55*, 612−619.

(1131) Gunnarsson, I.; Arnórsson, S. Amorphous Silica Solubility and the Thermodynamic Properties of H4sio°4 in the Range of 0° to 350°C at Psat. *Geochim. Cosmochim. Acta* **2000**, *64*, 2295−2307.

(1132) He, J.; Liu, M.; Huang, K.; Walker, T. W.; Maravelias, C. T.; Dumesic, J. A.; Huber, G. W. Production of Levoglucosenone and 5-Hydroxymethylfurfural from Cellulose in Polar Aprotic Solvent-Water Mixtures. *Green Chem.* **2017**, *19*, 3642−3653.

(1133) Krishna, S. H.; McClelland, D. J.; Rashke, Q. A.; Dumesic, J. A.; Huber, G. W. Hydrogenation of Levoglucosenone to Renewable Chemicals. *Green Chem.* **2017**, *19*, 1278−1285.

(1134) Kim, H.; Lee, S.; Won, W. System-Level Analyses for the Production of 1,6-Hexanediol from Cellulose. *Energy* **2021**, *214*, 118974.

(1135) Ahsan, M.; Sung, S.; Jeon, H.; Patil, M.; Chung, T.; Yun, H. Biosynthesis of Medium- to Long-Chain A,Ω-Diols from Free Fatty Acids Using Cyp153a Monooxygenase, Carboxylic Acid Reductase, and E. Coli Endogenous Aldehyde Reductases. *Catalysts* **2018**, *8*, 4−14.

(1136) Fujii, T.; Narikawa, T.; Sumisa, F.; Arisawa, A.; Takeda, K.; Kato, J. Production of A,Ω-Alkanediols Using Escherichia Coli Expressing a Cytochrome P450 from Acinetobacter Sp. Oc4. *Biosci. Biotechnol. Biochem.* **2006**, *70*, 1379−1385.

(1137) de Souza, F. M.; Kahol, P. K.; Gupta, R. K. Polyols from Sustainable Resources. In *Polyurethane Chemistry: Renewable Polyols and Isocyanates*; American Chemical Society, 2021; Vol. *1380*, pp 25−49.

(1138) Sardon, H.; Mecerreyes, D.; Basterretxea, A.; Avérous, L.; Jehanno, C. From Lab to Market: Current Strategies for the Production of Biobased Polyols. *ACS Sus. Chem. Eng.* **2021**, *9*, 10664−10677.

(1139) de Angelis, A.; Ingallina, P.; Perego, C. Solid Acid Catalysts for Industrial Condensations of Ketones and Aldehydes with Aromatics. *Ind. Eng. Chem. Res.* **2004**, *43*, 1169−1178.

(1140) Bu, Q.; Lei, H.; Ren, S.; Wang, L.; Holladay, J.; Zhang, Q.; Tang, J.; Ruan, R. Phenol and Phenolics from Lignocellulosic Biomass by Catalytic Microwave Pyrolysis. *Bioresour. Technol.* **2011**, *102*, 7004−7007.

(1141) Eladak, S.; Grisin, T.; Moison, D.; Guerquin, M.-J.; N'Tumba-Byn, T.; Pozzi-Gaudin, S.; Benachi, A.; Livera, G.; Rouiller-Fabre, V.; Habert, R. A New Chapter in the Bisphenol a Story: Bisphenol S and Bisphenol F Are Not Safe Alternatives to This Compound. *Fertil. Steril.* **2015**, *103*, 11−21.

(1142) Kose, O.; Rachidi, W.; Beal, D.; Erkekoglu, P.; Fayyad-Kazan, H.; Kocer Gumusel, B. The Effects of Different Bisphenol Derivatives on Oxidative Stress, DNA Damage and DNA Repair in Rwpe-1 Cells: A Comparative Study. *J. Appl. Toxic.* **2020**, *40*, 643−654.

(1143) Rochester, J. R.; Bolden, A. L. Bisphenol S and F: A Systematic Review and Comparison of the Hormonal Activity of Bisphenol a Substitutes. *Environ. Health Perspect.* **2015**, *123*, 643−650.

(1144) Perera, L.; Li, Y.; Coons, L. A.; Houtman, R.; van Beuningen, R.; Goodwin, B.; Auerbach, S. S.; Teng, C. T. Binding of Bisphenol a, Bisphenol Af, and Bisphenol S on the Androgen Receptor: Coregulator Recruitment and Stimulation of Potential Interaction Sites. *Toxic. in Vitro* **2017**, *44*, 287−302.

(1145) Liguori, F.; Moreno-Marrodan, C.; Barbaro, P. Biomass-Derived Chemical Substitutes for Bisphenol A: Recent Advancements in Catalytic Synthesis. *Chem. Soc. Rev.* **2020**, *49*, 6329−6363.

(1146) Garrison, M. D.; Storch, P. J.; Eck, W. S.; Adams, V. H.; Fedick, P. W.; Harvey, B. G. Bpa-Free High-Performance Sustainable Polycarbonates Derived from Non-Estrogenic Bio-Based Phenols. *Green Chem.* **2021**, *23*, 8016−8029.

(1147) Wang, X.; Gao, S.; Wang, J.; Xu, S.; Li, H.; Chen, K.; Ouyang, P. The Production of Biobased Diamines from Renewable Carbon Sources: Current Advances and Perspectives. *Chin. J. Chem. Eng.* **2021**, *30*, 4−13.

(1148) Lee, J.; Lee, Y.; Kim, S.; Kwon, E. E.; Lin, K.-Y. A. Catalytic Production of Hexamethylenediamine from Renewable Feedstocks. *Korean J. Chem. Eng.* **2021**, *38*, 1079−1086.

(1149) Coeck, R.; De Vos, D. E. One-Pot Reductive Amination of Carboxylic Acids: A Sustainable Method for Primary Amine Synthesis. *Green Chem.* **2020**, *22*, 5105−5114.

(1150) Deeba, M.; Ford, M. F.; Johnson, T. A. Production of Ethylene Diamine from Monoethanolamine and Ammonia. EP 0252425A2, 1988.

(1151) Roose, P.; Eller, K.; Henkes, E.; Rossbacher, R.; Höke, H. Amines, Aliphatic. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley VCH, 2015; pp 1−55.

(1152) Letellier, G.; Dumon-Seignovert, L.; Figge, R. Ethylenediamine Fermentative Production by a Recombinant Microorganism. WO 2014/049382, 2014.

(1153) Dasu, V. V.; Nakada, Y.; Ohnishi-Kameyama, M.; Kimura, K.; Itoh, Y. Characterization and a Role of Pseudomonas Aeruginosa Spermidine Dehydrogenase in Polyamine Catabolism. *Microbiology (Reading, Engl.)* **2006**, *152*, 2265−2272.

(1154) Ikai, H.; Yamamoto, S. Identification and Analysis of a Gene Encoding L-2,4-Diaminobutyrate:2-Ketoglutarate 4-Aminotransferase Involved in the 1,3-Diaminopropane Production Pathway in Acinetobacter Baumannii. *J. Bacteriol.* **1997**, *179*, 5118−5125.

(1155) Ikai, H.; Yamamoto, S. Cloning and Expression in Escherichia Coli of the Gene Encoding a Novel L-2,4-Diaminobutyrate Decarboxylase of Acinetobacter Baumannii. *Fems Microbiol. Lett.* **1994**, *124*, 225−228.

(1156) Wang, X.; Wang, W.; Liu, X.; Wang, Y. Amphoteric Functional Polymers for Leather Wet Finishing Auxiliaries: A Review. *Polym. Adv. Technol.* **2021**, *32*, 1951−1964.

(1157) Scott, E.; Peter, F.; Sanders, J. Biomass in the Manufacture of Industrial Products - the Use of Proteins and Amino Acids. *Appl. Microbiol. & Biotechnol.* **2007**, *75*, 751−762.

(1158) Schneider, J.; Wendisch, V. F. Putrescine Production by Engineered Corynebacterium Glutamicum. *Appl. Microbiol. & Biotechnol.* **2010**, *88*, 859−868.

(1159) Qian, Z.-G.; Xia, X.-X.; Lee, S. Y. Metabolic Engineering of Escherichia Coli for the Production of Putrescine: A Four Carbon Diamine. *Biotechnol. Bioeng.* **2009**, *104*, 651−662.

(1160) Minho, N.; Yoo, S. M.; Kim, W. J.; Lee, S. Y. Gene Expression Knockdown by Modulating Synthetic Small Rna Expression in Escherichia Coli. *Cell Syst.* **2017**, *5*, 418−426.

(1161) Schneider, J.; Eberhardt, D.; Wendisch, V. F. Improving Putrescine Production by Corynebacterium Glutamicum by Fine-Tuning Ornithine Transcarbamoylase Activity Using a Plasmid Addiction System. *Appl. Microbiol. & Biotechnol.* **2012**, *95*, 169−178.

(1162) Nguyen, A. Q. D.; Schneider, J.; Reddy, G. K.; Wendisch, V. F. Fermentative Production of the Diamine Putrescine: System Metabolic Engineering of Corynebacterium Glutamicum. *Metabolites* **2015**, *5*, 211−231.

(1163) Kim, H. J.; Kim, Y. H.; Shin, J.-H.; Bhatia, S. K.; Sathiyanarayanan, G.; Seo, H.-M.; Choi, K. Y.; Yang, Y.-H.; Park, K. Optimization of Direct Lysine Decarboxylase Biotransformation for Cadaverine Production with Whole-Cell Biocatalysts at High Lysine Concentration. *J. Microbiol. Biotechnol.* **2015**, *25*, 1108−1113.

(1164) Shin, J.; Joo, J. C.; Lee, E.; Hyun, S. M.; Kim, H. J.; Park, S. J.; Yang, Y.-H.; Park, K. Characterization of a Whole-Cell Biotransformation Using a Constitutive Lysine Decarboxylase from Escherichia Coli for the High-Level Production of Cadaverine from Industrial Grade L-Lysine. *Appl. Microbiol. Biotechnol.* **2018**, *185*, 909−924.

(1165) Kim, H. T.; Baritugo, K.-A.; Oh, Y. H.; Kang, K.-H.; Jung, Y. J.; Jang, S.; Song, B. K.; Kim, I.-K.; Lee, M. O.; Hwang, Y. T.; et al. High-Level Conversion of L-Lysine into Cadaverine by Escherichia

Coli Whole Cell Biocatalyst Expressing Hafnia Alvei L-Lysine Decarboxylase. *Polymers* **2019**, *11*, 1184.

(1166) Soksawatmaekhin, W.; Kuraishi, A.; Sakata, K.; Kashiwagi, K.; Igarashi, K. Excretion and Uptake of Cadaverine by Cadb and Its Physiological Functions in Escherichia Coli. *Mol. Microbiol.* **2004**, *51*, 1401−1412.

(1167) Choi, S.; Song, C. W.; Shin, J. H.; Lee, S. Y. Biorefineries for the Production of Top Building Block Chemicals and Their Derivatives. *Metab. Eng.* **2015**, *28*, 223−239.

(1168) Hafner, E. W.; Tabor, C. W.; Tabor, H. Mutants of Escherichia Coli That Do Not Contain 1,4-Diaminobutane (Putrescine) or Spermidine. *J. Biol. Chem.* **1979**, *254*, 12419−12426.

(1169) Qian, Z.-G.; Xia, X.-X.; Lee, S. Y. Metabolic Engineering of Escherichia Coli for the Production of Cadaverine: A Five Carbon Diamine. *Biotechnol. Bioeng.* **2011**, *108*, 93−103.

(1170) Na, D.; Yoo, S. M.; Chung, H.; Park, H.; Park, J. H.; Lee, S. Y. Metabolic Engineering of Escherichia Coli Using Synthetic Small Regulatory Rnas. *Nat. Biotechnol.* **2013**, *31*, 170−174.

(1171) Mimitsuka, T.; Sawai, H.; Hatsu, M.; Yamada, K. Metabolic Engineering of Corynebacterium Glutamicum for Cadaverine Fermentation. *Biosci. Biotechnol. Biochem.* **2007**, *71*, 2130−2135.

(1172) Kind, S.; Jeong, W. K.; Schroeder, H.; Wittmann, C. Systems-Wide Metabolic Pathway Engineering in Corynebacterium Glutamicum for Bio-Based Production of Diaminopentane. *Metab. Eng.* **2010**, *12*, 341−351.

(1173) Oh, Y. H.; Choi, J. W.; Kim, E. Y.; Song, B. K.; Jeong, K. J.; Park, K.; Kim, I.-K.; Woo, H. M.; Lee, S. H.; Park, S. J. Construction of Synthetic Promoter-Based Expression Cassettes for the Production of Cadaverine in Recombinant Corynebacterium Glutamicum. *Appl. Microbiol. Biotechnol.* **2015**, *176*, 2065−2075.

(1174) Buschke, N.; Schroeder, H.; Wittmann, C. Metabolic Engineering of Corynebacterium Glutamicum for Production of 1,5-Diaminopentane from Hemicellulose. *Biotechnol. J.* **2011**, *6*, 306−317.

(1175) Antoniewicz, M. R. Synthetic Methylotrophy: Strategies to Assimilate Methanol for Growth and Chemicals Production. *Curr. Opin. Biotechnol.* **2019**, *59*, 165−174.

(1176) Schrader, J.; Schilling, M.; Holtmann, D.; Sell, D.; Villela Filho, M.; Marx, A.; Vorholt, J. A. Methanol-Based Industrial Biotechnology: Current Status and Future Perspectives of Methylotrophic Bacteria. *Trends in Biotechnol.* **2009**, *27*, 107−115.

(1177) Behr, A. Methanol: The Basic Chemical and Energy Feedstock of the Future. Asinger's Vision Today. Edited by Martin Bertau, Heribert Offermanns, Ludolf Plass, Friedrich Schmidt and Hans-Jürgen Wernicke. *Angew. Chem., Int. Ed.* **2014**, *53*, 12674−12674.

(1178) Witthoff, S.; Schmitz, K.; Niedenfuehr, S.; Noeh, K.; Noack, S.; Bott, M.; Marienhagen, J. Metabolic Engineering of Corynebacterium Glutamicum for Methanol Metabolism. *Appl. Environ. Microbiol.* **2015**, *81*, 2215−2225.

(1179) Lessmeier, L.; Pfeifenschneider, J.; Carnicer, M.; Heux, S.; Portais, J.-C.; Wendisch, V. F. Production of Carbon-13-Labeled Cadaverine by Engineered Corynebacterium Glutamicum Using Carbon-13-Labeled Methanol as Co-Substrate. *Appl. Microbiol. & Biotechnol.* **2015**, *99*, 10163−10176.

(1180) Botes, A.; Conradie, A. V. E. Methods of Producing 6-Carbon Chemicals Via Coa-Dependent Carbon Chain Elongation Associated with Carbon Storage. US 9102958B2, 2015.

(1181) Balladur, V.; Fouilloux, P.; De Bellefon, C. Monometallic Ni, Co and Ru, and Bimetallic Nicr, Niti and Cofe Ziegler-Sloan-Lapporte Catalysts for the Hydrogenation of Adiponitrile into Hexamethylenediamine: Effect of Water and Dopants. *Appl. Catal. A: General* **1995**, *133*, 367−376.

(1182) Lee, Y. H.; Lee, S. W.; Kim, H. J.; Kim, Y. T.; Lin, K. Y. A.; Lee, J. C. Hydrogenation of Adiponitrile to Hexamethylenediamine over Raney Ni and Co Catalysts. *Appl. Sci. (Basel)* **2020**, *10*, 7506.

(1183) Li, H.; Xu, Y.; Deng, J.-F. Selective Hydrogenation of Adiponitrile over a Raney Ni-P Amorphous Catalyst. *New J. Chem.* **1999**, *23*, 1059−1061.

(1184) Harper, M. J. Raney Cobalt Catalyst and a Process for Hydrogenating Organic Compounds Using Said Catalyst. US 6156694, 2000.

(1185) Yu, X.; Li, H.; Deng, J.-F. Selective Hydrogenation of Adiponitrile over a Skeletal Ni-P Amorphous Catalyst (Raney Ni-P) at 1atm Pressure. *Appl. Catal. A: General* **2000**, *199*, 191−198.

(1186) Li, H.; Xu, Y.; Li, H.; Deng, J. F. Gas-Phase Hydrogenation of Adiponitrile with High Selectivity to Primary Amine over Supported Ni-B Amorphous Catalysts. *Appl. Catal. A: General* **2001**, *216*, 51−58.

(1187) Alini, S.; Bottino, A.; Capannelli, G.; Carbone, R.; Comite, A.; Vitulli, G. The Catalytic Hydrogenation of Adiponitrile to Hexamethylenediamine over a Rhodium/Alumina Catalyst in a Three Phase Slurry Reactor. *J. Mol. Catal. A: Chem.* **2003**, *206*, 363−370.

(1188) Matthieu, C.; Dietrich, E.; Delmas, H.; Jenck, J. Hydrogenation of Adiponitrile Catalyzed by Raney Nickel Use of Intrinsic Kinetics to Measure Gas-Liquid Mass Transfer in a Gas Induced Stirred Slurry Reactor. *Chem. Eng. Sci.* **1992**, *47*, 2289−2294.

(1189) Joly-Vuillemin, C.; Gavroy, D.; Cordier, G.; De Bellefon, C.; Delmas, H. Three-Phase Hydrogenation of Adiponitrile Catalyzed by Raney Nickel: Kinetic Model Discrimination and Parameter Optimization. *Chem. Eng. Sci.* **1994**, *49*, 4839−4849.

(1190) Cole-Hamilton, D. J. Homogeneous Catalysis-New Approaches to Catalyst Separation, Recovery, and Recycling. *Science* **2003**, *299*, 1702−6.

(1191) Dev, A.; Srivastava, A. K.; Karmakar, S. New Generation Hybrid Nanobiocatalysts. In *Handbook of Nanomaterials for Industrial Applications*; Elsevier, 2018; pp 217−231.

(1192) Tolman, C. A. Steric and Electronic Effects in Olefin Hydrocyanation at Du Pont: A Scientific and Industrial Success Story. *J. Chem. Educ.* **1986**, *63*, 199.

(1193) Shu, X.; Jiang, Y.-Y.; Kang, L.; Yang, L. Ni-Catalyzed Hydrocyanation of Alkenes with Formamide as the Cyano Source. *Green Chem.* **2020**, *22*, 2734−2738.

(1194) Rostrup-Nielsen, J. R. Chemistry. Making Fuels from Biomass. *Science* **2005**, *308*, 1421−2.

(1195) Goldemberg, J. Ethanol for a Sustainable Energy Future. *Science* **2007**, *315*, 808−10.

(1196) Ohnishi, R.; Akimoto, T.; Tanabe, K. Pronounced Catalytic Activity and Selectivity of Mgo-Sio2-Na2o for Synthesis of Buta-1,3-Diene from Ethanol. *J. Chem. Soc., Chem. Commun.* **1985**, 1613−1614.

(1197) Chieregato, A.; Ochoa, J. V.; Bandinelli, C.; Fornasari, G.; Cavani, F.; Mella, M. On the Chemistry of Ethanol on Basic Oxides: Revising Mechanisms and Intermediates in the Lebedev and Guerbet Reactions. *ChemSusChem* **2015**, *8*, 377−388.

(1198) Ochoa, J. V.; Bandinelli, C.; Vozniuk, O.; Chieregato, A.; Malmusi, A.; Recchi, C.; Cavani, F. An Analysis of the Chemical, Physical and Reactivity Features of Mgo-Sio2 Catalysts for Butadiene Synthesis with the Lebedev Process. *Green Chem.* **2016**, *18*, 1653−1663.

(1199) Pomalaza, G.; Capron, M.; Ordomsky, V.; Dumeignil, F. Recent Breakthroughs in the Conversion of Ethanol to Butadiene. *Catalysts* **2016**, *6*, 203.

(1200) Kyriienko, P. I.; Larina, O. V.; Soloviev, S. O.; Orlyk, S. M.; Calers, C.; Dzwigaj, S. Ethanol Conversion into 1,3-Butadiene by the Lebedev Method over Mtasibea Zeolites (M = Ag, Cu, Zn). *ACS Sus. Chem. Eng.* **2017**, *5*, 2075−2083.

(1201) Sheldon, R. A. Green and Sustainable Manufacture of Chemicals from Biomass: State of the Art. *Green Chem.* **2014**, *16*, 950−963.

(1202) Zeitsch, K. J. *The Chemistry and Technology of Furfural and Its Many by-Products*; Elsevier, 2000.

(1203) Lange, J.-P.; Van Der Heide, E.; Van Buijtenen, J.; Price, R. Furfural-a Promising Platform for Lignocellulosic Biofuels. *ChemSusChem* **2012**, *5*, 150−166.

(1204) Deshpande, R. M.; Buwa, V. V.; Rode, C. V.; Chaudhari, R. V.; Mills, P. L. Tailoring of Activity and Selectivity Using Bimetallic Catalyst in Hydrogenation of Succinic Acid. *Catal. Commun.* **2002**, *3*, 269−274.

(1205) Kang, K. H.; Hong, U. G.; Bang, Y.; Choi, J. H.; Kim, J. K.; Lee, J. K.; Han, S. J.; Song, I. K. Hydrogenation of Succinic Acid to 1,4-Butanediol over Re-Ru Bimetallic Catalysts Supported on Mesoporous Carbon. *Appl. Catal. A: General* **2015**, *490*, 153−162.

(1206) Zhang, W.; Zhu, Y.; Niu, S.; Li, Y. A Study of Furfural Decarbonylation on K-Doped Pd/Al2o3 Catalysts. *J. Mol. Catal. A: Chem.* **2011**, *335*, 71−81.

(1207) Ishida, T.; Kume, K.; Kinjo, K.; Honma, T.; Nakada, K.; Ohashi, H.; Yokoyama, T.; Hamasaki, A.; Murayama, H.; Izawa, Y.; et al. Efficient Decarbonylation of Furfural to Furan Catalyzed by Zirconia-Supported Palladium Clusters with Low Atomicity. *ChemSusChem* **2016**, *9*, 3441−3447.

(1208) Pushkarev, V. V.; Musselwhite, N.; An, K.; Alayoglu, S.; Somorjai, G. A. High Structure Sensitivity of Vapor-Phase Furfural Decarbonylation/Hydrogenation Reaction Network as a Function of Size and Shape of Pt Nanoparticles. *Nano Lett.* **2012**, *12*, 5196−5201.

(1209) An, K.; Musselwhite, N.; Kennedy, G.; Pushkarev, V. V.; Robert Baker, L.; Somorjai, G. A. Preparation of Mesoporous Oxides and Their Support Effects on Pt Nanoparticle Catalysts in Catalytic Hydrogenation of Furfural. *J. Colloid Interface Sci.* **2013**, *392*, 122−128.

(1210) Fischer, R.; Pinkos, R. Method of Producing 1,4-Butanediol and Tetrahydrofuran from Furan. US 5905159, 1999.

(1211) Wang, Y. C.; Sun, D. L.; Yamada, Y.; Sato, S. Selective Production of 1,3-Butadiene in the Dehydration of 1,4-Butanediol over Rare Earth Oxides. *Appl. Catal. A: General* **2018**, *562*, 11−18.

(1212) Nakagawa, Y.; Kasumi, T.; Ogihara, J.; Tamura, M.; Arai, T.; Tomishige, K. Erythritol: Another C4 Platform Chemical in Biomass Refinery. *ACS Omega* **2020**, *5*, 2520−2530.

(1213) Childers, K. G.; Dreher, S. D.; Lee, J.; Williams, J. M. A Practical and Scaleable Preparation of 1,4-Anhydroerythritol. *Org. Process Res. Dev.* **2006**, *10*, 934−936.

(1214) Liu, L. J.; Asano, T.; Nakagawa, Y.; Tamura, M.; Tomishige, K. One-Pot Synthesis of 1,3-Butanediol by 1,4-Anhydroerythritol Hydrogenolysis over a Tungsten-Modified Platinum on Silica Catalyst. *Green Chem.* **2020**, *22*, 2375−2380.

(1215) Jing, F.; Katryniok, B.; Araque, M.; Wojcieszak, R.; Capron, M.; Paul, S.; Daturi, M.; Clacens, J. M.; De Campo, F.; Liebens, A.; et al. Direct Dehydration of 1,3-Butanediol into Butadiene over Aluminosilicate Catalysts. *Catal. Sci. Technol.* **2016**, *6*, 5830−5840.

(1216) Dai, J.-J.; Huang, Y.-B.; Fang, C.; Guo, Q.-X.; Fu, Y. Electrochemical Synthesis of Adiponitrile from the Renewable Raw Material Glutamic Acid. *ChemSusChem* **2012**, *5*, 617−620.

(1217) Liu, H.; Guo, Y.; Yu, Y. S.; Yang, W. W.; Shen, M. Q.; Liu, X. Y.; Geng, S.; Li, J. R.; Yu, C.; Yin, Z. Y.; et al. Surface Pd-Rich Pdag Nanowires as Highly Efficient Catalysts for Dehydrogenation of Formic Acid and Subsequent Hydrogenation of Adiponitrile. *J. Mater. Chem. A* **2018**, *6*, 17323−17328.

(1218) Horlenko, T.; Tatum, H. W. Process for the Preparation of Alkylene Diamines. US 3215742, 1965.

(1219) Decker, M.; Schmidt, J.; Hoffman, H.; Pistor, H. J. Manufacture of Adiponitrile. US 3671566, 1972.

(1220) Musser, M. T. *Adipic Acid*; Wiley-VCH, 2000.

(1221) Baldwin, J. E.; North, M.; Flinn, A.; Moloney, M. G. Synthesis of Nonproteinogenic Amino Acids Part 2. Preparation of a Synthetic Equivalent of the Gamma Anion Synthon for Asymmetric Amino Acid Synthesis. *Tetra.* **1989**, *45*, 1453−1464.

(1222) Blanco, D. E.; Dookhith, A. Z.; Modestino, M. A. Enhancing Selectivity and Efficiency in the Electrochemical Synthesis of Adiponitrile. *React. Chem. Eng.* **2019**, *4*, 8−16.

(1223) Wang, C. Q.; Jia, Z. K.; Zhen, B.; Han, M. H. Supported Ni Catalyst for Liquid Phase Hydrogenation of Adiponitrile to 6-Aminocapronitrile and Hexamethyenediamine. *Molecules* **2018**, *23*, 92.

(1224) de Bellefon, C.; Fouilloux, P. Homogeneous and Heterogeneous Hydrogenation of Nitriles in a Liquid Phase: Chemical, Mechanistic, and Catalytic Aspects. *Catal. Rev.* **1994**, *36*, 459−506.

(1225) Howk, B. W. Catalytic Hydrogenation of Adiponitriles to Produce Hexamethylenediamines. US 2166151, 1939.

(1226) Augustine, R. L. Organic Functional Group Hydrogenation. *Catal. Rev.* **1976**, *13*, 285−316.

(1227) Herzog, B. D.; Smiley, R. A. Hexamethylenediamine. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH, 2000; pp 8012−8022.

(1228) Sengupta, S. K.; Augur Koch, T.; Krause, K. R. Process for Continuous Hydrogenation of Adiponitrile. US 5900511, 1999.

(1229) Gilkey, M. J.; Xu, B. J. Heterogeneous Catalytic Transfer Hydrogenation as an Effective Pathway in Biomass Upgrading. *ACS Catal.* **2016**, *6*, 1420−1436.

(1230) Van Putten, R.-J.; Soetedjo, J. N. M.; Pidko, E. A.; Van Der Waal, J. C.; Hensen, E. J. M.; De Jong, E.; Heeres, H. J. Dehydration of Different Ketoses and Aldoses to 5-Hydroxymethylfurfural. *ChemSusChem* **2013**, *6*, 1681−1687.

(1231) Nikolla, E.; Román-Leshkov, Y.; Moliner, M.; Davis, M. E. One-Pot" Synthesis of 5-(Hydroxymethyl)Furfural from Carbohydrates Using Tin-Beta Zeolite. *ACS Catal.* **2011**, *1*, 408−410.

(1232) Pagán-Torres, Y. J.; Wang, T.; Gallo, J. M. R.; Shanks, B. H.; Dumesic, J. A. Production of 5-Hydroxymethylfurfural from Glucose Using a Combination of Lewis and Brønsted Acid Catalysts in Water in a Biphasic Reactor with an Alkylphenol Solvent. *ACS Catal.* **2012**, *2*, 930−934.

(1233) Xu, S. Q.; Yin, C. Y.; Pan, D. H.; Hu, F.; Wu, Y. F.; Miao, Y. A.; Gao, L. J.; Xiao, G. M. Efficient Conversion of Glucose into 5-Hydroxymethylfurfural Using a Bifunctional Fe3+ Modified Amberlyst-15 Catalyst. *Sus. Energy & Fuels* **2019**, *3*, 390−395.

(1234) Dias, E. L.; Shoemaker, J. A. W.; Boussie, T. R.; Murphy, V. J. Process for Production of Hexamethylenediamine from Carbohydrate-Containing Materials and Intermediates Therefor. US 9518005, 2016.

(1235) Muller, C.; Bock, M.; Da Silva, M.; Fischer, R.-F.; Blank, B.; Kindler, A.; Melder, J.-P.; Otto, B.; Schelwies, M.; Henninger, A. Method for Producing Hexamethylenediamine. US 2016/0326092 A1, 2016.

(1236) Thaore, V.; Chadwick, D.; Shah, N. Sustainable Production of Chemical Intermediates for Nylon Manufacture: A Techno-Economic Analysis for Renewable Production of Caprolactone. *Chem. Eng. Res. Des.* **2018**, *135*, 140−152.

(1237) Dros, A. B.; Larue, O.; Reimond, A.; De Campo, F.; Pera-Titus, M. Hexamethylenediamine (Hmda) from Fossil- Vs. Bio-Based Routes: An Economic and Life Cycle Assessment Comparative Study. *Green Chem.* **2015**, *17*, 4760−4772.

(1238) Sung, S.; Jeon, H.; Sarak, S.; Ahsan, M. M.; Patil, M. D.; Kroutil, W.; Kim, B.-G.; Yun, H. Parallel Anti-Sense Two-Step Cascade for Alcohol Amination Leading to -Amino Fatty Acids and,-Diamines. *Green Chem.* **2018**, *20*, 4591−4595.

(1239) Mckeever, C. H.; Washburne, R. N. Process for the Preparation of Menthane Diamine. US 2955138A, 1960.

(1240) Harmsen, P. F. H.; Hackmann, M. M.; Bos, H. L. Green Building Blocks for Bio-Based Plastics. *Biofuels, Bioprod. & Bioref.* **2014**, *8*, 306−324.

(1241) Croda Priamine Dimer Diamines. https://www.crodasmartmaterials.com/en-gb/brands/priamine (accessed 23/03/2022).

(1242) Borges da Silva, E. A.; Zabkova, M.; Araujo, J. D.; Cateto, C. A.; Barreiro, M. F.; Belgacem, M. N.; Rodrigues, A. E. An Integrated Process to Produce Vanillin and Lignin-Based Polyurethanes from Kraft Lignin. *Chem. Eng. Res. Des.* **2009**, *87*, 1276−1292.

(1243) Araujo, J. D. P.; Grande, C. A.; Rodrigues, A. E. Vanillin Production from Lignin Oxidation in a Batch Reactor. *Chem. Eng. Res. Des.* **2010**, *88*, 1024−1032.

(1244) Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S.; Cramail, H. Selective Laccase-Catalyzed Dimerization of Phenolic Compounds Derived from Lignin: Towards Original Symmetrical Bio-Based (Bis) Aromatic Monomers. *J. Mol. Catal. B: Enzymatic* **2016**, *125*, 34−41.

(1245) Fache, M.; Darroman, E.; Besse, V.; Auvergne, R.; Caillol, S.; Boutevin, B. Vanillin, a Promising Biobased Building-Block for Monomer Synthesis. *Green Chem.* **2014**, *16*, 1987−1998.

(1246) Savonnet, E.; Le Coz, C.; Grau, E.; Grelier, S.; Defoort, B.; Cramail, H. Divanillin-Based Aromatic Amines: Synthesis and Use as Curing Agents for Fully Vanillin-Based Epoxy Thermosets. *Front. Chem.* **2019**, *7*, 606.

(1247) Voirin, C.; Caillol, S.; Sadavarte, N. V.; Tawade, B. V.; Boutevin, B.; Wadgaonkar, P. P. Functionalization of Cardanol: Towards Biobased Polymers and Additives. *Polym. Chem.* **2014**, *5*, 3142−3162.

(1248) Froidevaux, V.; Negrell, C.; Caillol, S.; Pascault, J.-P.; Boutevin, B. Biobased Amines: From Synthesis to Polymers; Present and Future. *Chem. Rev.* **2016**, *116*, 14181−14224.

(1249) Hamid, M. H. S. A.; Slatford, P. A.; Williams, J. M. J. Borrowing Hydrogen in the Activation of Alcohols. *Advanced Synthesis & Catalysis* **2007**, *349*, 1555−1575.

(1250) Shingte, R. D.; Tawade, B. V.; Wadgaonkar, P. P. Partially Biobased Processable Polyimides Based on Aromatic Diamine Derived from Cardanol. *Green Mater.* **2017**, *5*, 74−84.

(1251) Sadavarte, N. V.; Halhalli, M. R.; Avadhani, C. V.; Wadgaonkar, P. P. Synthesis and Characterization of New Polyimides Containing Pendent Pentadecyl Chains. *Eur. Polym. J.* **2009**, *45*, 582−589.

(1252) Garrison, M. D.; Harvey, B. G. Bio-Based Hydrophobic Epoxy-Amine Networks Derived from Renewable Terpenoids. *J. Appl. Polym. Sci.* **2016**, *133*, 43621.

(1253) Kreye, O.; Mutlu, H.; Meier, M. A. R. Sustainable Routes to Polyurethane Precursors. *Green Chem.* **2013**, *15*, 1431.

(1254) Randall, D. L. S. *The Polyurethanes Book*; [Huntsman Polyurethanes], Distributed by John Wiley & Sons, 2002.

(1255) Knölker, H.-J.; Braxmeier, T. Isocyanates, Part 4. Convenient Phosgene-Free Method for the Synthesis and Derivatization of Enantiopure A-Isocyanato Carboxylic Acid Esters. *Synlett* **1997**, *1997*, 925−928.

(1256) Slotta, K.; Lorenz, L. Über Isocyanate, L: Darstellung Aliphatischer Isocyanate. *Ber. Dtsch. Chem. Ges* **1925**, *58*, 1320−1323.

(1257) Akhlaghinia, B. A New and Convenient Method of Generating Alkyl Isocyanates from Alcohols, Thiols and Trimethylsilyl Ethers Using Triphenylphosphine/2, 3-Dichloro-5, 6-Dicyanobenzoquinone/Bu4nocn. *Synth.* **2005**, *2005*, 1955−1958.

(1258) Delebecq, E.; Pascault, J.-P.; Boutevin, B.; Ganachaud, F. On the Versatility of Urethane/Urea Bonds: Reversibility, Blocked Isocyanate, and Non-Isocyanate Polyurethane. *Chem. Rev.* **2013**, *113*, 80−118.

(1259) Chaturvedi, D. Perspectives on the Synthesis of Organic Carbamates. *Tetra.* **2012**, *68*, 15−45.

(1260) Ragaini, F. Away from Phosgene: Reductive Carbonylation of Nitroarenes and Oxidative Carbonylation of Amines, Understanding the Mechanism to Improve Performance. *J. Chem. Soc., Dalton Trans.* **2009**, 6251−6266.

(1261) Ragaini, F.; Cenini, S. Mechanistic Study of the Ru3 (Co) 12/Chloride Catalyzed Carbonylation Reactions of Nitroarenes to Carbamates and Ureas; the Role of the Alkylammonium Cation. *J. Mol. Catal. A: Chem.* **2000**, *161*, 31−38.

(1262) Ferretti, F.; Ragaini, F.; Lariccia, R.; Gallo, E.; Cenini, S. New Nonsymmetric Phenanthrolines as Very Effective Ligands in the Palladium-Catalyzed Carbonylation of Nitrobenzene. *Organometallics* **2010**, *29*, 1465−1471.

(1263) Kim, J.-H.; Kim, D.-W.; Cheong, M.-S.; Kim, H.-S.; Mukherjee, D. K. Catalytic Activity of Supported Rhodium (I) Complex for the Carbonylation of Nitrobenzene: Mechanism for Carbamate Formation. *Bull. Korean Chem. Soc.* **2010**, *31*, 1621−1627.

(1264) Zhang, X.; Jing, H.; Zhang, G. Selenium-Catalyzed Oxidative Carbonylation of Aniline and Alcohols to N-Phenylcarbamates. *Synth. Commun.* **2010**, *40*, 1614−1624.

(1265) Le, H. V.; Ganem, B. A Practical Synthesis of Isocyanates from Isonitriles: Ethyl 2-Isocyanatoacetate. *Org. Synth.* **2003**, *89*, 404−408.

(1266) Habibi, D.; Nasrollahzadeh, M.; Sahebekhtiari, H. Green Synthesis of Formamides Using the Natrolite Zeolite as a Natural, Efficient and Recyclable Catalyst. *J. Mol. Catal. A: Chem.* **2013**, *378*, 148−155.

(1267) Waibel, K. A.; Nickisch, R.; Möhl, N.; Seim, R.; Meier, M. A. R. A More Sustainable and Highly Practicable Synthesis of Aliphatic Isocyanides. *Green Chem.* **2020**, *22*, 933−941.

(1268) Butler, D. C. D.; Alper, H. Synthesis of Isocyanates from Carbamate Esters Employing Boron Trichloride. *Chem. Commun.* **1998**, 2575−2576.

(1269) Dashkin, R.; Kolesnikov, G.; Tsygankov, P.; Lebedev, I.; Lebedev, A.; Menshutina, N.; Ghafurov, K.; Bagomedov, A. Modeling of Isocyanate Synthesis by the Thermal Decomposition of Carbamates. *Computation* **2020**, *8*, 89.

(1270) Sureshbabu, V. V.; Patil, B. S.; Venkataramanarao, R. Preparation, Isolation, and Characterization of Nα-Fmoc-Peptide Isocyanates: Solution Synthesis of Oligo-A-Peptidyl Ureas. *J. Org. Chem.* **2006**, *71*, 7697−7705.

(1271) Tada, T.; Ishida, Y.; Saigo, K. Synthesis of 2, 2-[60] Fullerenoalkylamines Via the Curtius Rearrangement. *Synlett* **2007**, *2007*, 0235−0238.

(1272) Yoshimura, A.; Luedtke, M. W.; Zhdankin, V. V. (Tosylimino) Phenyl-Λ3-Iodane as a Reagent for the Synthesis of Methyl Carbamates Via Hofmann Rearrangement of Aromatic and Aliphatic Carboxamides. *J. Org. Chem.* **2012**, *77*, 2087−2091.

(1273) Simon, M.; Csunderlik, C.; Cotarca, L.; Căproiu, M. T.; Neda, I.; Turoczi, M. C.; Volpicelli, R. Synthesis of New Active O-Nitrophenyl Carbamates. *Synth. Commun.* **2005**, *35*, 1471−1479.

(1274) Sureshbabu, V. V.; Hemantha, H. Efficient Synthesis of N-Fmoc-Aminoalkoxy Pentafluorophenyl Carbonates: Application for the Synthesis of Oligopeptidyl Carbamates. *Synth. Commun.* **2009**, *39*, 3555−3566.

(1275) Han, C.; Porco Jr, J. A. Synthesis of Carbamates and Ureas Using Zr (Iv)-Catalyzed Exchange Processes. *Org. Lett.* **2007**, *9*, 1517−1520.

(1276) Reixach, E.; Bonet, N.; Rius-Ruiz, F. X.; Wershofen, S.; Vidal-Ferran, A. Zinc Acetates as Efficient Catalysts for the Synthesis of Bis-Isocyanate Precursors. *Ind. Eng. Chem. Res.* **2010**, *49*, 6362−6366.

(1277) Sun, D.-L.; Xie, S.-J.; Deng, J.-R.; Huang, C.-J.; Ruckenstein, E.; Chao, Z.-S. Ch 3 Coona as an Effective Catalyst for Methoxycarbonylation of 1, 6-Hexanediamine by Dimethyl Carbonate to Dimethylhexane-1, 6-Dicarbamate. *Green Chem.* **2010**, *12*, 483−490.

(1278) Firdaus, M.; Meier, M. A. Renewable Polyamides and Polyurethanes Derived from Limonene. *Green Chem.* **2013**, *15*, 370−380.

(1279) Mutlu, H.; Ruiz, J.; Solleder, S. C.; Meier, M. A. Tbd Catalysis with Dimethyl Carbonate: A Fruitful and Sustainable Alliance. *Green Chem.* **2012**, *14*, 1728−1735.

(1280) Pei, Y.; Li, H.; Liu, H.; Zhang, Y. Kinetic Study of Methoxycarbonylation of Methylene Dianiline with Dimethyl Carbonate Using Lead Acetate Catalyst. *Ind. Eng. Chem. Res.* **2011**, *50*, 1955−1961.

(1281) Pozo, M.; Gotor, V. Chiral Carbamates through an Enzymatic Alkoxycarbonylation Reaction. *Tetra.* **1993**, *49*, 4321−4326.

(1282) Lavandera, I.; Fernández, S.; Ferrero, M.; Gotor, V. First Regioselective Enzymatic Alkoxycarbonylation of Primary Amines. Synthesis of Novel 5 ‘-and 3 ‘-Carbamates of Pyrimidine 3 ‘, 5 ‘-Diaminonucleoside Derivatives Including Bvdu Analogues. *J. Org. Chem.* **2004**, *69*, 1748−1751.

(1283) Selva, M.; Tundo, P.; Perosa, A.; Dall'Acqua, F. Synthesis of Methyl Carbamates from Primary Aliphatic Amines and Dimethyl Carbonate in Supercritical Co2: Effects of Pressure and Cosolvents and Chemoselectivity. *J. Org. Chem.* **2005**, *70*, 2771−2777.

(1284) Kreye, O.; Wald, S.; Meier, M. A. Introducing Catalytic Lossen Rearrangements: Sustainable Access to Carbamates and Amines. *Advanced Synthesis & Catalysis* **2013**, *355*, 81−86.

(1285) Chaturvedi, D.; Chaturvedi, A. K.; Mishra, N.; Mishra, V. Triton-B-Catalyzed, Efficient, One-Pot Synthesis of Carbazates through Alcoholic Tosylates. *Synth. Commun.* **2008**, *38*, 4013−4022.

(1286) Cardona, F.; Soldaini, G.; Goti, A. Methyltrioxorhenium-Catalyzed Oxidation of Aromatic Aldoximes. *Synlett* **2004**, *2004*, 1553−1556.

(1287) Kumar, G. S.; Maheswari, C. U.; Kumar, R. A.; Kantam, M. L.; Reddy, K. R. Copper-Catalyzed Oxidative C−O Coupling by Direct C−H Bond Activation of Formamides: Synthesis of Enol Carbamates and 2-Carbonyl-Substituted Phenol Carbamates. *Angew. Chem., Int. Ed.* **2011**, *50*, 11748−11751.

(1288) Patil, Y. P.; Tambade, P. J.; Jagtap, S. R.; Bhanage, B. M. Carbon Dioxide: A Renewable Feedstock for the Synthesis of Fine and Bulk Chemicals. *Front. Chem. Eng. China* **2010**, *4*, 213−235.

(1289) Fujita, S.-i.; Bhanage, B. M.; Ikushima, Y.; Arai, M. Synthesis of Dimethyl Carbonate from Carbon Dioxide and Methanol in the Presence of Methyl Iodide and Base Catalysts under Mild Conditions: Effect of Reaction Conditions and Reaction Mechanism. *Green Chem.* **2001**, *3*, 87−91.

(1290) Honda, M.; Suzuki, A.; Noorjahan, B.; Fujimoto, K.-i.; Suzuki, K.; Tomishige, K. Low Pressure Co2 to Dimethyl Carbonate by the Reaction with Methanol Promoted by Acetonitrile Hydration. *Chem. Commun.* **2009**, 4596−4598.

(1291) Eta, V.; Maki-Arvela, P.; Leino, A.-R.; Kordás, K.; Salmi, T.; Murzin, D. Y.; Mikkola, J.-P. Synthesis of Dimethyl Carbonate from Methanol and Carbon Dioxide: Circumventing Thermodynamic Limitations. *Ind. Eng. Chem. Res.* **2010**, *49*, 9609−9617.

(1292) Zhang, Z.-F.; Liu, Z.-W.; Lu, J.; Liu, Z.-T. Synthesis of Dimethyl Carbonate from Carbon Dioxide and Methanol over Cexzr1-Xo2 and [Emim]Br/Ce0.5zr0.5o2. *Ind. Eng. Chem. Res.* **2011**, *50*, 1981−1988.

(1293) Ballivet-Tkatchenko, D.; Bernard, F.; Demoisson, F.; Plasseraud, L.; Sanapureddy, S. R. Tin-Based Mesoporous Silica for the Conversion of Co2 into Dimethyl Carbonate. *ChemSusChem* **2011**, *4*, 1316−1322.

(1294) Zhu, D.; Mei, F.; Chen, L.; Li, T.; Mo, W.; Li, G. Synthesis of Dimethyl Carbonate by Oxidative Carbonylation Using an Efficient and Recyclable Catalyst Co- Schiff Base/Zeolite. *Energy Fuels* **2009**, *23*, 2359−2363.

(1295) Itoh, H.; Watanabe, Y.; Mori, K.; Umino, H. Synthesis of Dimethyl Carbonate by Vapor Phase Oxidative Carbonylation of Methanol. *Green Chem.* **2003**, *5*, 558−562.

(1296) Rebmann, G.; Keller, V.; Ledoux, M. J.; Keller, N. Cu-Y Zeolite Supported on Silicon Carbide for the Vapour Phase Oxidative Carbonylation of Methanol to Dimethyl Carbonate. *Green Chem.* **2008**, *10*, 207−213.

(1297) Bhanage, B. M.; Fujita, S.-i.; Ikushima, Y.; Arai, M. Transesterification of Urea and Ethylene Glycol to Ethylene Carbonate as an Important Step for Urea Based Dimethyl Carbonate Synthesis. *Green Chem.* **2003**, *5*, 429−432.

(1298) Wang, M.; Zhao, N.; Wei, W.; Sun, Y. Synthesis of Dimethyl Carbonate from Urea and Methanol over Zno. *Ind. Eng. Chem. Res.* **2005**, *44*, 7596−7599.

(1299) Zhao, W.; Wang, F.; Peng, W.; Zhao, N.; Li, J.; Xiao, F.; Wei, W.; Sun, Y. Synthesis of Dimethyl Carbonate from Methyl Carbamate and Methanol with Zinc Compounds as Catalysts. *Ind. Eng. Chem. Res.* **2008**, *47*, 5913−5917.

(1300) Zhang, C.; Lu, B.; Wang, X.; Zhao, J.; Cai, Q. Selective Synthesis of Dimethyl Carbonate from Urea and Methanol over Fe 2 O 3/Hmcm-49. *Catal. Sci. Technol.* **2012**, *2*, 305−309.

(1301) Bhanage, B. M.; Fujita, S.-i.; Ikushima, Y.; Torii, K.; Arai, M. Synthesis of Dimethyl Carbonate and Glycols from Carbon Dioxide, Epoxides and Methanol Using Heterogeneous Mg Containing Smectite Catalysts: Effect of Reaction Variables on Activity and Selectivity Performance. *Green Chem.* **2003**, *5*, 71−75.

(1302) Wang, J.-Q.; Sun, J.; Shi, C.-Y.; Cheng, W.-G.; Zhang, X.-P.; Zhang, S.-J. Synthesis of Dimethyl Carbonate from Co 2 and Ethylene Oxide Catalyzed by K 2 Co 3-Based Binary Salts in the Presence of H 2 O. *Green Chem.* **2011**, *13*, 3213−3217.

(1303) Wei, T.; Wang, M.; Wei, W.; Sun, Y.; Zhong, B. Synthesis of Dimethyl Carbonate by Transesterification over Cao/Carbon Composites. *Green Chem.* **2003**, *5*, 343−346.

(1304) Tian, J.-S.; Miao, C.-X.; Wang, J.-Q.; Cai, F.; Du, Y.; Zhao, Y.; He, L.-N. Efficient Synthesis of Dimethyl Carbonate from Methanol, Propylene Oxide and Co 2 Catalyzed by Recyclable Inorganic Base/Phosphonium Halide-Functionalized Polyethylene Glycol. *Green Chem.* **2007**, *9*, 566−571.

(1305) Abimanyu, H.; Ahn, B. S.; Kim, C. S.; Yoo, K. S. Preparation and Characterization of Mgo- Ceo2Mixed Oxide Catalysts by Modified Coprecipitation Using Ionic Liquids for Dimethyl Carbonate Synthesis. *Ind. Eng. Chem. Res.* **2007**, *46*, 7936−7941.

(1306) Juárez, R.; Corma, A.; García, H. Gold Nanoparticles Promote the Catalytic Activity of Ceria for the Transalkylation of Propylene Carbonate to Dimethyl Carbonate. *Green Chem.* **2009**, *11*, 949−952.

(1307) Yan, C.; Lu, B.; Wang, X.; Zhao, J.; Cai, Q. Electrochemical Synthesis of Dimethyl Carbonate from Methanol, Co2 and Propylene Oxide in an Ionic Liquid. *J. Chem. Technol. Biotechnol.* **2011**, *86*, 1413−1417.

(1308) Textile Exchange. *Preferred Fiber & Materials Market Report 2021*; Textile Exchange, 2021.

(1309) Coca-Cola Sustainable Packaging. https://www.coca-colacompany.com/sustainable-business/packaging-sustainability (accessed 23/03/2022).

(1310) Barnard, E.; Rubio Arias, J. J.; Thielemans, W. Chemolytic Depolymerisation of Pet: A Review. *Green Chem.* **2021**, *23*, 3765−3789.

(1311) Coca-Cola Coca-Cola Collaborates with Tech Partners to Create Bottle Prototype Made from 100% Plant-Based Sources. https://www.coca-colacompany.com/news/100-percent-plant-based-plastic-bottle (accessed 21/03/2022).

(1312) Fei, X.; Wang, J.; Zhang, X.; Jia, Z.; Jiang, Y.; Liu, X. Recent Progress on Bio-Based Polyesters Derived from 2,5-Furandicarbonxylic Acid (Fdca). *Polymers (Basel)* **2022**, *14*, 625.

(1313) Rhim, J.-W. Preparation and Characterization of Vacuum Sputter Silver Coated Pla Film. *LWT - Food Sci. Technol.* **2013**, *54*, 477−484.

(1314) Ye, H.-M.; Wang, R.-D.; Liu, J.; Xu, J.; Guo, B.-H. Isomorphism in Poly(Butylene Succinate-Co-Butylene Fumarate) and Its Application as Polymeric Nucleating Agent for Poly(Butylene Succinate). *Macromolecules* **2012**, *45*, 5667−5675.

(1315) Rafiqah, S. A.; Khalina, A.; Harmaen, A. S.; Tawakkal, I. A.; Zaman, K.; Asim, M.; Nurrazi, M. N.; Lee, C. H. A Review on Properties and Application of Bio-Based Poly(Butylene Succinate). *Polymers (Basel)* **2021**, *13*, 1436.

(1316) Bautista, M.; Martínez de Ilarduya, A.; Alla, A.; Vives, M.; Morató, J.; Muñoz-Guerra, S. Cationic Poly(Butylene Succinate) Copolyesters. *Eur. Polym. J.* **2016**, *75*, 329−342.

(1317) Xu, J.; Guo, B.-H. Microbial Succinic Acid, Its Polymer Poly(Butylene Succinate), and Applications. In *Plastics from Bacteria: Natural Functions and Applications*; Chen, G. G.-Q., Ed.; Springer: Berlin, Heidelberg, 2010; pp 347−388.

(1318) Ramos, M.; Jiménez, A.; Peltzer, M.; Garrigós, M. C. Development of Novel Nano-Biocomposite Antioxidant Films Based on Poly (Lactic Acid) and Thymol for Active Packaging. *Food Chem.* **2014**, *162*, 149−155.

(1319) Li, H.; Chang, J.; Cao, A.; Wang, J. In Vitro Evaluation of Biodegradable Poly(Butylene Succinate) as a Novel Biomaterial. *Macromol. Biosci.* **2005**, *5*, 433−440.

(1320) Gomes, M.; Gandini, A.; Silvestre, A. J. D.; Reis, B. Synthesis and Characterization of Poly(2,5-Furan Dicarboxylate)S Based on a Variety of Diols. *J. Polym. Sci. A: Polym. Chem.* **2011**, *49*, 3759−3768.

(1321) Gandini, A.; Lacerda, T. M.; Carvalho, A. J. F.; Trovatti, E. Progress of Polymers from Renewable Resources: Furans, Vegetable Oils, and Polysaccharides. *Chem. Rev.* **2016**, *116*, 1637−1669.

(1322) Jiang, M.; Liu, Q.; Zhang, Q.; Ye, C.; Zhou, G. A Series of Furan-Aromatic Polyesters Synthesized Via Direct Esterification

Method Based on Renewable Resources. *J. Polym. Sci. A: Polym. Chem.* **2012**, *50*, 1026−1036.

(1323) Banella, M. B.; Bonucci, J.; Vannini, M.; Marchese, P.; Lorenzetti, C.; Celli, A. Insights into the Synthesis of Poly(Ethylene 2,5-Furandicarboxylate) from 2,5-Furandicarboxylic Acid: Steps toward Environmental and Food Safety Excellence in Packaging Applications. *Ind. Eng. Chem. Res.* **2019**, *58*, 8955−8962.

(1324) Burgess, S. K.; Karvan, O.; Johnson, J. R.; Kriegel, R. M.; Koros, W. J. Oxygen Sorption and Transport in Amorphous Poly(Ethylene Furanoate). *Polymer* **2014**, *55*, 4748−4756.

(1325) Burgess, S. K.; Kriegel, R. M.; Koros, W. J. Carbon Dioxide Sorption and Transport in Amorphous Poly(Ethylene Furanoate). *Macromolecules* **2015**, *48*, 2184−2193.

(1326) Burgess, S. K.; Leisen, J. E.; Kraftschik, B. E.; Mubarak, C. R.; Kriegel, R. M.; Koros, W. J. Chain Mobility, Thermal, and Mechanical Properties of Poly(Ethylene Furanoate) Compared to Poly(Ethylene Terephthalate). *Macromolecules* **2014**, *47*, 1383−1391.

(1327) Avantium Fdca and Plantmeg Together Make a 100% Plant-Based Plastic Pef. https://www.avantium.com/lead-products/#pef&fdca/ (accessed 21/03/2022).

(1328) Dortland, C. c. R. Avantium Acquires the Right to Use Eastman's Fdca-Related Patent Portfolio; Avantium, 2021.

(1329) Maltsev, A. PEF Challenges Pet to Battle. https://ethz.ch/en/news-and-events/eth-news/news/2018/07/pef-for-pet.html (accessed 23/03/2022).

(1330) Rosenboom, J.-G.; Hohl, D. K.; Fleckenstein, P.; Storti, G.; Morbidelli, M. Bottle-Grade Polyethylene Furanoate from Ring-Opening Polymerisation of Cyclic Oligomers. *Nat. Commun.* **2018**, *9*, 2701.

(1331) Zhu, J.; Cai, J.; Xie, W.; Chen, P.-H.; Gazzano, M.; Scandola, M.; Gross, R. A. Poly(Butylene 2,5-Furan Dicarboxylate), a Biobased Alternative to Pbt: Synthesis, Physical Properties, and Crystal Structure. *Macromolecules* **2013**, *46*, 796−804.

(1332) Tsanaktsis, V.; Papageorgiou, G. Z.; Bikiaris, D. N. A Facile Method to Synthesize High-Molecular-Weight Biobased Polyesters from 2,5-Furandicarboxylic Acid and Long-Chain Diols. *J. Polym. Sci. A: Polym. Chem.* **2015**, *53*, 2617−2632.

(1333) Lomelí-Rodríguez, M.; Corpas-Martínez, J. R.; Willis, S.; Mulholland, R.; Lopez-Sanchez, J. A. Synthesis and Characterization of Renewable Polyester Coil Coatings from Biomass-Derived Isosorbide, Fdca, 1,5-Pentanediol, Succinic Acid, and 1,3-Propanediol. *Polymers* **2018**, *10*, 600.

(1334) Chen, J.; Lin, Y.; Chen, Y.; Koning, C. E.; Wu, J.; Wang, H. Low-Crystallinity to Highly Amorphous Copolyesters with High Glass Transition Temperatures Based on Rigid Carbohydrate-Derived Building Blocks. *Polym. Internat.* **2021**, *70*, 536−545.

(1335) Ahn, J. H.; Lee, J. A.; Bang, J.; Lee, S. Y. Membrane Engineering Via Trans-Unsaturated Fatty Acids Production Improves Succinic Acid Production in Mannheimia Succiniciproducens. *J. Ind. Microbiol. Biotechnol.* **2018**, *45*, 555−566.

(1336) PlasticsEurope. *Plastics- the Facts, 2021*; PlasticsEurope, 2021.

(1337) Brehmer, B. *Polyamides from Biomass Derived Monomers*; Wiley, 2013; p 275−293.

(1338) Hower, M. *Rennovia Develops Process to Produce 100% Bio-Based Nylon*; SustainableBrands.com, 2013; Vol. *2022*.

(1339) de Duzman, D. *Bio-Based Chems Market Sees Setback with Rennovia Exit*; Green Chemicals Blog: 2018; Vol. *2022*.

(1340) Sherman, L. M. *Genomatica and Asahi Kasei Collaborate on Renewably-Sourced Nylon 66*. Plastics Technology: 2022; Vol. *2022*.

(1341) Chemicals, D.The Past, Future and Present of the Polyamide Industry. https://www.domochemicals.com/en/media/news/past-future-and-present-polyamide-industry (accessed 21/03/2022).

(1342) Zhang, Y.; Wang, Y.; Xu, Y.; Liu, X.; Guo, W. Modification of Biobased Polyamide 56 to Achieve Ultra-Toughening. *Polym.-Plast. Technol. Mater.* **2021**, *60*, 1−20.

(1343) Francisco, D. L.; Paiva, L. B.; Aldeia, W. Advances in Polyamide Nanocomposites: A Review. *Polym. Comp.* **2019**, *40*, 851−870.

(1344) Stojšić, J.; Raos, P.; Kalendova, A. A Study of Structure and Tensile Properties of Polyamide 12/Clay Nanocomposites. *Polym. Comp.* **2016**, *37*, 684−691.

(1345) Battegazzore, D.; Sattin, A.; Maspoch, M. L.; Frache, A. Mechanical and Barrier Properties Enhancement in Film Extruded Bio-Polyamides with Modified Nanoclay. *Polym. Comp.* **2019**, *40*, 2617−2628.

(1346) Mutua, F. N.; Cheng, C.; Dong, Y.; Zheng, C.; Zhu, B.; He, Y. Synthesis and Properties of Bio-Based Poly(Pentamethylene Oxamide). *Polym. Eng. Sci.* **2018**, *58*, 659−664.

(1347) Lee, J. A.; Ahn, J. H.; Kim, I.; Li, S.; Lee, S. Y. Synthesis, Characterization, and Application of Fully Biobased and Biodegradable Nylon-4,4 and -5,4. *ACS Sus. Chem. Eng.* **2020**, *8*, 5604−5614.

(1348) Yang, P.; Li, X.; Liu, H.; Li, Z.; Liu, J.; Zhuang, W.; Wu, J.; Ying, H. Thermodynamics, Crystal Structure, and Characterization of a Bio-Based Nylon 54 Monomer. *CrystEngComm* **2019**, *21*, 7069−7077.

(1349) Li, H.; Shang, Y.; Huang, W.; Xue, B.; Zhang, X.; Cui, Z.; Fu, P.; Pang, X.; Zhao, Q.; Liu, M. Synthesis of Succinic Acid-Based Polyamide through Direct Solid-State Polymerization Method: Avoiding Cyclization of Succinic Acid. *J. Appl. Polym. Sci.* **2021**, *138*, 51017.

(1350) Zhang, Q.; Luo, X. L.; Zhang, M. L.; Wang, X. J.; Zhang, G.; Long, S. R.; Yang, J. Mechanical and Thermomechanical Properties of Nylon6t/66/Pps Blends. *Mater. Sci. Forum* **2015**, *815*, 503−508.

(1351) Shen, T.; Zhang, B.; Wang, Y.; Yang, P.; Li, M.; Hu, R.; Guo, K.; Chen, K.; Zhu, N.; Wang, L.; et al. Production of 100% Bio-Based Semi-Aromatic Nylon by Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid with Bio Aliphatic Diamine. *Chem. Eng. J.* **2022**, *437*, 135361.

(1352) Fernandez, L. *Global Polyurethane Market Vol. 2015-2021*; Statista, 2021.

(1353) Zdrahala, R. J.; Zdrahala, I. J. Biomedical Applications of Polyurethanes: A Review of Past Promises, Present Realities, and a Vibrant Future. *J. Biomater. Appl.* **1999**, *14*, 67−90.

(1354) Thomson, T. *Polyurethanes as Specialty Chemicals: Principles and Applications*; CRC Press, 2004.

(1355) Matsumura, S.; Soeda, Y.; Toshima, K. Perspectives for Synthesis and Production of Polyurethanes and Related Polymers by Enzymes Directed toward Green and Sustainable Chemistry. *Appl. Microbiol. & Biotechnol.* **2006**, *70*, 12−20.

(1356) Darensbourg, D. J.; Horn Jr, A.; Moncada, A. I. A Facile Catalytic Synthesis of Trimethylene Carbonate from Trimethylene Oxide and Carbon Dioxide. *Green Chem.* **2010**, *12*, 1376−1379.

(1357) Khatoon, H.; Iqbal, S.; Irfan, M.; Darda, A.; Rawat, N. K. A Review on the Production, Properties and Applications of Non-Isocyanate Polyurethane: A Greener Perspective. *Prog. Org. Coat.* **2021**, *154*, 106124.

(1358) Gomez-Lopez, A.; Panchireddy, S.; Grignard, B.; Calvo, I.; Jerome, C.; Detrembleur, C.; Sardon, H. Poly(Hydroxyurethane) Adhesives and Coatings: State-of-the-Art and Future Directions. *ACS Sus. Chem. Eng.* **2021**, *9*, 9541−9562.

(1359) Hahn, C.; Keul, H.; Möller, M. Hydroxyl-Functional Polyurethanes and Polyesters: Synthesis, Properties and Potential Biomedical Application. *Polym. Internat.* **2012**, *61*, 1048−1060.

(1360) Guan, J.; Song, Y.; Lin, Y.; Yin, X.; Zuo, M.; Zhao, Y.; Tao, X.; Zheng, Q. Progress in Study of Non-Isocyanate Polyurethane. *Ind. Eng. Chem. Res.* **2011**, *50*, 6517−6527.

(1361) Figovsky, O. L.; Shapovalov, L. D. Features of Reaction Amino-Cyclocarbonate for Production of New Type Nonisocyanate Polyurethane Coatings. *Macromol. Symp.* **2002**, *187*, 325−332.

(1362) Hernández, A.; Houck, H. A.; Elizalde, F.; Guerre, M.; Sardon, H.; Du Prez, F. E. Internal Catalysis on the Opposite Side of the Fence in Non-Isocyanate Polyurethane Covalent Adaptable Networks. *Eur. Polym. J.* **2022**, *168*, 111100.

(1363) Rokicki, G.; Piotrowska, A. A New Route to Polyurethanes from Ethylene Carbonate, Diamines and Diols. *Polymer* **2002**, *43*, 2927−2935.

(1364) Neffgen, S.; Kušan, J.; Fey, T.; Keul, H.; Höcker, H. Synthesis and Thermal Properties of [N]-Polyurethanes. *Macromol. Chem. Phys.* **2000**, *201*, 2108−2114.

(1365) Bhanage, B. M.; Fujita, S.-i.; Ikushima, Y.; Arai, M. Synthesis of Cyclic Ureas and Urethanes from Alkylene Diamines and Amino Alcohols with Pressurized Carbon Dioxide in the Absence of Catalysts. *Green Chem.* **2003**, *5*, 340−342.

(1366) Sakakura, T.; Choi, J.-C.; Yasuda, H. Transformation of Carbon Dioxide. *Chem. Rev.* **2007**, *107*, 2365−2387.

(1367) Ihata, O.; Kayaki, Y.; Ikariya, T. Synthesis of Thermoresponsive Polyurethane from 2-Methylaziridine and Supercritical Carbon Dioxide. *Angew. Chem., Int. Ed.* **2004**, *43*, 717−719.

(1368) Ihata, O.; Kayaki, Y.; Ikariya, T. Control of Thermoresponsive Behavior of Poly (Urethane-Amine) S Prepared by Copolymerization of Supercritical Carbon Dioxide and Aziridines. *J. Appl. Polym. Sci.* **2005**, *62*, 196−199.

(1369) Bähr, M.; Bitto, A.; Mülhaupt, R. Cyclic Limonene Dicarbonate as a New Monomer for Non-Isocyanate Oligo- and Polyurethanes (Nipu) Based Upon Terpenes. *Green Chem.* **2012**, *14*, 1447−1454.

(1370) Mahendran, A. R.; Aust, N.; Wuzella, G.; Müller, U.; Kandelbauer, A. Bio-Based Non-Isocyanate Urethane Derived from Plant Oil. *J. Polym. Environ.* **2012**, *20*, 926−931.

(1371) Boyer, A.; Cloutet, E.; Tassaing, T.; Gadenne, B.; Alfos, C.; Cramail, H. Solubility in Co2 and Carbonation Studies of Epoxidized Fatty Acid Diesters: Towards Novel Precursors for Polyurethane Synthesis. *Green Chem.* **2010**, *12*, 2205−2213.

(1372) Deepa, P.; Jayakannan, M. Solvent-Free and Nonisocyanate Melt Transurethane Reaction for Aliphatic Polyurethanes and Mechanistic Aspects. *J. Polym. Sci. A: Polym. Chem.* **2008**, *46*, 2445−2458.

(1373) Shi, R.; Jiang, S.; Cheng, H.; Wu, P.; Zhang, C.; Arai, M.; Zhao, F. Synthesis of Polyurea Thermoplastics through a Non-isocyanate Route Using Co2 and Aliphatic Diamines. *ACS Sus. Chem. Eng.* **2020**, *8*, 18626−18635.

(1374) Ritter, B. S.; Mülhaupt, R. Isocyanate- and Solvent-Free Route to Thermoplastic Poly(Amide-Urea) Derived from Renewable Resources. *Macromol. Mater. Eng.* **2017**, *302*, 1600338.

(1375) Ban, J.-L.; Li, S.-Q.; Yi, C.-F.; Zhao, J.-B.; Zhang, Z.-Y.; Zhang, J.-Y. Amorphous and Crystallizable Thermoplastic Polyureas Synthesized through a One-Pot Non-Isocyanate Route. *Chin. J. Polym. Sci.* **2019**, *37*, 43−51.

(1376) Qaroush, A. K.; Al-Hamayda, A. S.; Khashman, Y. K.; Vagin, S. I.; Troll, C.; Rieger, B. Highly Efficient Isocyanate-Free Microwave-Assisted Synthesis of [6]-Oligourea. *Catal. Sci. Technol.* **2013**, *3*, 2221−2226.

(1377) Qaroush, A. K.; Castillo-Molina, D. A.; Troll, C.; Abu-Daabes, M. A.; Alsyouri, H. M.; Abu-Surrah, A. S.; Rieger, B. [N]-Oligourea-Based Green Sorbents with Enhanced Co2 Sorption Capacity. *ChemSusChem* **2015**, *8*, 1618−1626.

(1378) Ma, S.; Liu, C.; Sablong, R. J.; Noordover, B. A. J.; Hensen, E. J. M.; van Benthem, R. A. T. M.; Koning, C. E. Catalysts for Isocyanate-Free Polyurea Synthesis: Mechanism and Application. *ACS Catal.* **2016**, *6*, 6883−6891.

(1379) Ma, S.; van Heeswijk, E. P. A.; Noordover, B. A. J.; Sablong, R. J.; van Benthem, R. A. T. M.; Koning, C. E. Isocyanate-Free Approach to Water-Borne Polyurea Dispersions and Coatings. *ChemSusChem* **2018**, *11*, 149−158.

(1380) Ma, S.; Chen, C.; Sablong, R. J.; Koning, C. E.; van Benthem, R. A. T. M. Non-Isocyanate Strategy for Anionically Stabilized Water-Borne Polyurea Dispersions and Coatings. *J. Polym. Sci. A: Polym. Chem.* **2018**, *56*, 1078−1090.

(1381) Li, S.; Sang, Z.; Zhao, J.; Zhang, Z.; Zhang, J.; Yang, W. Crystallizable and Tough Aliphatic Thermoplastic Polyureas Synthesized through a Nonisocyanate Route. *Ind. Eng. Chem. Res.* **2016**, *55*, 1902−1911.

(1382) Wang, P.; Ma, X.; Li, Q.; Yang, B.; Shang, J.; Deng, Y. Green Synthesis of Polyureas from Co2 and Diamines with a Functional Ionic Liquid as the Catalyst. *RSC Adv.* **2016**, *6*, 54013−54019.

(1383) Jiang, S.; Shi, R.; Cheng, H.; Zhang, C.; Zhao, F. Synthesis of Polyurea from 1,6-Hexanediamine with Co2 through a Two-Step Polymerization. *Green Energy Environ.* **2017**, *2*, 370−376.

(1384) Wang, P.; Fei, Y.; Long, Y.; Deng, Y. Catalytic Polymerization of Co2 to Polyureas over K3po4 Catalyst. *J. CO2 Util.* **2018**, *28*, 403−407.

(1385) Wu, P.-X.; Cheng, H.-Y.; Shi, R.-H.; Jiang, S.; Wu, Q.-F.; Zhang, C.; Arai, M.; Zhao, F.-Y. Synthesis of Polyurea Via the Addition of Carbon Dioxide to a Diamine Catalyzed by Organic and Inorganic Bases. *Advanced Synthesis & Catalysis* **2019**, *361*, 317−325.

(1386) Wang, P.; Fei, Y.; Deng, Y. Transformation of Co2 into Polyureas with 3-Amino-1,2,4-Triazole Potassium as a Solid Base Catalyst. *New J. Chem.* **2018**, *42*, 1202−1207.

(1387) Yamazaki, N.; Higashi, F.; Iguchi, T. Polyureas and Polythioureas from Carbon Dioxide and Disulfide with Diamines under Mild Conditions. *J. Polym. Sci.: Polym. Lett.* **1974**, *12*, 517−521.

(1388) Rokicki, G. Direct Method of Synthesis of Polyureas by N-Acylphosphoramidites. *Makromol. Chem.* **1988**, *189*, 2513−2520.

(1389) Wu, C.; Wang, J.; Chang, P.; Cheng, H.; Yu, Y.; Wu, Z.; Dong, D.; Zhao, F. Polyureas from Diamines and Carbon Dioxide: Synthesis, Structures and Properties. *Phys. Chem. Chem. Phys.* **2012**, *14*, 464−468.

(1390) Ying, Z.; Zhao, L.; Zhang, C.; Yu, Y.; Liu, T.; Cheng, H.; Zhao, F. Utilization of Carbon Dioxide to Build a Basic Block for Polymeric Materials: An Isocyanate-Free Route to Synthesize a Soluble Oligourea. *RSC Adv.* **2015**, *5*, 42095−42100.

(1391) Wu, P.; Cheng, H.; Wang, Y.; Shi, R.; Wu, Z.; Arai, M.; Zhao, F. New Kind of Thermoplastic Polyurea Elastomers Synthesized from Co2 and with Self-Healing Properties. *ACS Sus. Chem. Eng.* **2020**, *8*, 12677−12685.

(1392) Tang, D.; Mulder, D. J.; Noordover, B. A.; Koning, C. E. Well-Defined Biobased Segmented Polyureas Synthesis Via a Tbd-Catalyzed Isocyanate-Free Route. *Macromol. Rap. Commun.* **2011**, *32*, 1379−1385.

(1393) Santana, J. S.; Cardoso, E. S.; Triboni, E. R.; Politi, M. J. Polyureas Versatile Polymers for New Academic and Technological Applications. *Polymers* **2021**, *13*, 4393.

(1394) Brunelle, D. J.; Korn, M. R. *Advances in Polycarbonates*; ACS Publications, 2005.

(1395) Odian, G. *Principles of Polymerization*; John Wiley & Sons, 2004.

(1396) Morin, N.; Arp, H. P. H.; Hale, S. E. Bisphenol a in Solid Waste Materials, Leachate Water, and Air Particles from Norwegian Waste-Handling Facilities: Presence and Partitioning Behavior. *Environ. Sci. Technol.* **2015**, *49*, 7675−7683.

(1397) Su, W.; Zhong, W.; Bian, G.; Shi, X.; Zhang, J. Recent Advances in the Chemistry of Trichloromethyl Chloroformate and Bis-(Trichloromethyl) Carbonate. *Org. Prep. Proced. Int.* **2004**, *36*, 499−547.

(1398) Garcia-Martin, M. G.; Perez, R. R.; Hernandez, E. B.; Espartero, J. L.; Munoz-Guerra, S.; Galbis, J. A. Carbohydrate-Based Polycarbonates. Synthesis, Structure, and Biodegradation Studies. *Macromolecules* **2005**, *38*, 8664−8670.

(1399) Koelewijn, S. F.; Van den Bosch, S.; Renders, T.; Schutyser, W.; Lagrain, B.; Smet, M.; Thomas, J.; Dehaen, W.; Van Puyvelde, P.; Witters, H.; et al. Sustainable Bisphenols from Renewable Softwood Lignin Feedstock for Polycarbonates and Cyanate Ester Resins. *Green Chem.* **2017**, *19*, 2561−2570.

(1400) Harvey, B. G.; Guenthner, A. J.; Yandek, G. R.; Cambrea, L. R.; Meylemans, H. A.; Baldwin, L. C.; Reams, J. T. Synthesis and Characterization of a Renewable Cyanate Ester/Polycarbonate Network Derived from Eugenol. *Polymer* **2014**, *55*, 5073−5079.

(1401) Noel, A.; Borguet, Y. P.; Raymond, J. E.; Wooley, K. L. Poly(Carbonate-Amide)S Derived from Bio-Based Resources: Poly-(Ferulic Acid-Co-Tyrosine). *Macromolecules* **2014**, *47*, 2974−2983.

(1402) Koelewijn, S.-F.; Ruijten, D.; Trullemans, L.; Renders, T.; Van Puyvelde, P.; Witters, H.; Sels, B. F. Regioselective Synthesis, Isomerisation, in Vitro Oestrogenic Activity, and Copolymerisation of Bisguaiacol F (Bgf) Isomers. *Green Chem.* **2019**, *21*, 6622−6633.

(1403) Gong, J.; Ma, X.; Wang, S. Phosgene-Free Approaches to Catalytic Synthesis of Diphenyl Carbonate and Its Intermediates. *Appl. Catal. A: General* **2007**, *316*, 1−21.
(1404) Lingier, S.; Spiesschaert, Y.; Dhanis, B.; De Wildeman, S.; Du Prez, F. E. Rigid Polyurethanes, Polyesters, and Polycarbonates from Renewable Ketal Monomers. *Macromolecules* **2017**, *50*, 5346−5352.
(1405) Choi, G.-H.; Hwang, D. Y.; Suh, D. H. High Thermal Stability of Bio-Based Polycarbonates Containing Cyclic Ketal Moieties. *Macromolecules* **2015**, *48*, 6839−6845.
(1406) Harvey, B. G.; Guenthner, A. J.; Koontz, T. A.; Storch, P. J.; Reams, J. T.; Groshens, T. J. Sustainable Hydrophobic Thermosetting Resins and Polycarbonates from Turpentine. *Green Chem.* **2016**, *18*, 2416−2423.
(1407) Liu, X.; Pang, C.; Ma, J.; Gao, H. Random Copolycarbonates Based on a Renewable Bicyclic Diol Derived from Citric Acid. *Macromolecules* **2017**, *50*, 7949−7958.
(1408) Durand, P.-L.; Brege, A.; Chollet, G.; Grau, E.; Cramail, H. A Simple and Efficient Approach toward Photosensitive Biobased Aliphatic Polycarbonate Materials. *ACS Macro Lett.* **2018**, *7*, 250−254.
(1409) Hauenstein, O.; Reiter, M.; Agarwal, S.; Rieger, B.; Greiner, A. Bio-Based Polycarbonate from Limonene Oxide and Co2 with High Molecular Weight, Excellent Thermal Resistance, Hardness and Transparency. *Green Chem.* **2016**, *18*, 760−770.