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Processing of agricultural apple fruit waste into sugar rich feedstocks for the catalytic production of 5-HMF over a Sn Amberlyst-15 resin catalyst

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ABSTRACT

In this study we considered processes of treatment of agricultural apple waste which is normally discarded. We show the effect of various pre-treatment procedures on the final catalytic performance to produce 5-HMF from this real world biomass waste. Our study of the various potential pre-treatment steps, and their effect on the catalytic performance, provides valuable new insights which can be used for the development of new processes for the localised small scale valorization of agricultural fruit waste. The apple waste is aimed to be converted into a sugar rich feedstock stream for the catalytic conversion to 5-hydroxymethyl furfural (5-HMF) at low temperatures ($\sim 120^\circ\text{C}$). Filters with varying pore sizes were studied for the filtration of apple pomace after milling the rotten apples in order to reduce the solids content. The tested filters varied in pore sizes of $0.2\ \mu\text{m}$, $2\ \mu\text{m}$ and $54\ \mu\text{m}$. The effect of heating, acid or base treatment of the apple slurry was evaluated for increasing the speed of filtration. The highest flow rate was obtained for the filter with $54\ \mu\text{m}$ pores. The sugar rich filtrates were investigated in the catalytic conversion to 5-HMF over an easy-to-manufacture Sn exchanged resin (Amberlyst-15) catalyst. Results showed that filtrates obtained over a $2\ \mu\text{m}$ filter lead to the highest 5-HMF yields (18 %) without extra additives. Adjustment of the reaction mixtures to pH 7 resulted in a lower catalytic activity. 5-HMF is proposed to be extracted from the aqueous layer by using an organic liquid layer (methyl isobutyl ketone, MIBK). In order to increase the diffusion of 5-HMF to the MIBK layer the addition of salts to the reaction mixture was investigated. This leads to lower catalytic activity, possibly due to catalyst deactivation. Our results showed that a relatively wide pore filter ($54\ \mu\text{m}$) provides the fastest apple processing method and a filtrate reacting to the highest 5-HMF yield in catalytic conversion of the sugar rich product stream obtained from agricultural waste apples.

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Introduction

The current trend in the chemical industry is to shift from mineral oil-based feedstocks to biorenewable alternatives. Drivers for this movement is the reduction of carbon footprint by reducing the emission of CO_2 . The current generation of chemical products is based on the use of fossil feedstocks for their production. Furthermore, in order to refine fossil feedstocks such as mineral oil energy intensive processes are required emitting vast amounts

of CO_2 . The use of biobased feedstocks can potentially reduce the carbon footprint of the production of valuable chemical products. One of the potential replacements for the benzene, toluene and xylene (BTX) manufacture is the platform molecule; 5-hydroxymethylfurfural (5-HMF) which can be derived from renewable resources [1] and produced via various routes [2]. The molecule 5-HMF can be produced from carbohydrates (glucose, fructose and cellulose) via a chemo-catalytic route extensively discussed in literature over variety of heterogeneous catalysts [3–7]. When starting from glucose, the carbohydrate needs to be isomerized to fructose over Lewis acidic sites (LAS) after which the fructose is dehydrated to 5-HMF of the Brønsted acid sites (BAS) [8–10]. Recently, we have reported a cheap and easy-to-manufacture

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catalyst based on an acidic resin exchanged with tin chloride (Sn(II)Cl₂) with high activity for the glucose to 5-HMF conversion [11]. The present catalyst shows good activity at process temperatures as low as 120 °C.

Since carbohydrates are abundant in nature as (hemi-)cellulose and free sugars in many fruits, 5-HMF can be an interesting alternative platform molecule for the transition of the chemical industry [12]. Many research papers discuss the production of 5-HMF from wood derived cellulose which can be a clean bulk source of glucose carbohydrates [13–16]. Such resources are of interest to produce bulk products like plastics (e.g. polyethylenefuranoate, PEF). However, agriculture produces a large volume of waste containing high volumes of carbohydrate feedstock in the form of (hemi-)cellulose and free sugars [17–19]. The latter group can be found in high concentrations in fruit waste in the form of glucose, fructose and sucrose [20]. A large agricultural sector in the Netherlands is apple farming which produces a substantial stream of apples not suitable for sale due to inconsistencies (e.g. rotten spots) [21]. The use of such feedstocks due to strongly varying compositions and batch volumes is not suitable for the production of bulk products like plastics, but more for the production of fine chemicals and pharmaceutical ingredients [22,23].

Unlike dedicated crops, such as sugar cane and beet streams as a source of carbohydrates, the use of second-generation biomass (e.g. rotten apples) is substantially more challenging due to the complex composition of the feedstock material. The biomass needs to be hydrolysed to break the polysaccharides such as cellulose to monosaccharides. Furthermore, the remaining solids need to be separated from the product stream (sugar water), which potentially lead to problems when applying such feedstocks into a process. Gullón et al. [20] have analysed the contents of apples into detail and showed the composition of apples to be a complex mixture of proteins, lipids, phenolics, minerals and vitamins. In this study we consider apples to be divided in two components, apple juice and apple pomace which mainly consists of (hemi-)cellulosic and lignin. The high solid content of apples could lead to adsorption to the catalyst surface and, thus leads to catalyst deactivation. Also, feeding the highly viscous slurry obtained by processing the apples could lead to mechanical blocking of the catalytic reactor. This necessitates the removal of solid content from the slurry before feeding the sugar rich liquor feedstock to the reactor. In order to reduce the solid content and increase the monosaccharide content an additional hydrolysis step is beneficial. A study by Parmar and Rupasingha [24] discusses the effect of an acid treatment with diluted acid to reduce the cellulose content in biomass waste.

In this study we identified the effects of various pre-treatment approaches of biomass waste from apple farming on the catalytic conversion of the sugar rich feedstock to 5-HMF. Our results on these effects could help to develop processes for the local production of 5-HMF from sugar rich agricultural waste streams. Many studies have investigated the use of model reaction mixtures using pure sugars. However, in order to develop new processes for the conversion of realistic sugar rich biomass mixtures the treatment of real biomass into a sugar rich feedstock and the catalytic evaluation is essential. Especially the low temperature conversion (120 °C) using cheap catalyst systems could enable the local conversion of agricultural waste into high value chemicals such as 5-HMF which can be used as starting material to produce pharmaceutical ingredients and fine chemicals. In this study, we investigate and discuss a promising route to process solid apples into a sugar rich feedstock which can be catalytically converted to 5-HMF at low temperatures. Fig. 1 shows a schematic representation of the different steps for the upgrading of apple waste material to 5-HMF. In route A, the mixture after milling is directly filtered and neutralised before the clear filtrate is converted to 5-HMF,

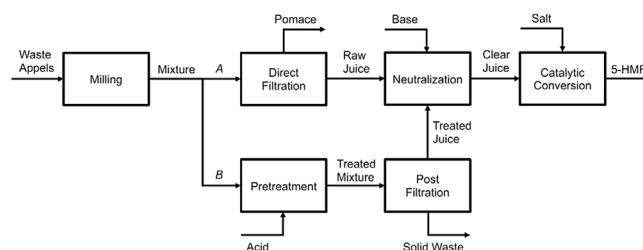


Fig. 1. Flow diagram for the upgrading of rotten apples into a sugar rich feedstock for the low temperature catalytic conversion to 5-HMF.

while in route B the mixture is pre-treated before the filtration and neutralisation. We discuss the effect of filter type and prefiltration hydrolysis of the apple waste biomass on the catalytic conversion of the recovered sugars towards 5-HMF. For the filtration of apple pomace and apple juice we have investigated two types of filtration, namely fine pore (0.2 µm pores), medium pore (2 µm pores) and large pore filtration (54 µm pores). For the hydrolysis of the prefiltered apple slurry, we investigated the influence of heating and acid or base addition. We also report the effect of neutralization of the filtrates and the effect of salt addition on the catalytic performance. Increasing the pH to 7 could allow the use of cheaper materials to withstand corrosion and could prevent the undesired side reactions which could potentially cause catalyst deactivation. The addition of salt has been reported to be beneficial for the transfer of HMF from the water phase to the methyl isobutyl ketone (MIBK) phase [25,26]. For the catalytic evaluation we use the resin catalyst that is one times exchanged with Sn(II)Cl₂. This resin catalyst we have reported earlier [11] which has shown excellent performance for the conversion of glucose, fructose and sucrose sugars to HMF at low temperatures (120 °C).

Experimental

Filtration experiments

For the preparation of the mixture by milling, typically 1500 g of solid apple material weighed. The apples were cut into 4 parts and put in the blender (Vitamix Total Nutrition Center, 2 L) at a blade cutting speed of 32,000 rpm. The collected slurry is denoted as AS, acronym for Apple Slurry. A part (1000 mL) of the apple slurry was diluted with water in a 1.0:1.3 AS to water ratio. The diluted apple mixture is named as AS_Diluted.

A part (500 mL) of the diluted apple mixture was filtered via various filtration types. One part was filtered using a ceramic candle filter (Labortherm, 0.2 µm pores) which was connected to a glass laboratory water jet pump to create a vacuum over the system. The apple juice filtrates collected according this method are denoted as “AF_0.2 µm”. Another part (500 mL) of the diluted apple slurry was filtered using a fabric filter (SEFAR TETEX mono, 05-1001-SK-054, 54 µm pores). These filtrate samples are denoted as “AF_54 µm”. Another part of the diluted apple pomace was filtered over a paper filter with 2 µm pores (Schleiger & Schüll, blue band 589/3). The apple juice filtrates collected according this method are denoted as “AF_2 µm”. All slurry and filtrate samples were stored in the refrigerator.

The pH was measured using a Metrohm 913 pH meter. Prior to the measurement the apparatus was calibrated using Merck buffers of pH 4.00, pH 7.00 and pH 10.00. The liquid samples were left to warm to ambient temperatures before the pH measurements were conducted.

The solid contents of the various slurries, filtrates and residues obtained after filtration by weighing before and after drying the

samples. To be able to determine the dry solid content samples were dried in an oven overnight at a set temperature of 120 °C.

Neutralization experiments

For the neutralization of the apple filtrates (raw and treated juice) 0.1 M NaOH (Merck) and 1 M Na₂CO₃ (Merck) aqueous solutions were prepared. Typically, 10 mL of filtrate was neutralized using either the NaOH or Na₂CO₃ solution. The pH was monitored using a 913 Metrohm pH meter.

Catalytic evaluation

For the evaluation of the catalysts in batch mode, typically 2 mL of apple filtrate solution (clear juice) and 2 mL methyl isobutyl ketone (MIBK, Merck) were added into an Ace Glass pressure tube #7 (rated 150 psi). Into each reaction tube 300 mg of catalyst was added. The Sn containing catalyst was prepared according to the 1 time exchange procedure reported earlier [9] which has been extensively characterized in this report and is from the same batch as reported there. The catalyst is denoted as “1xSn-Amb”. After adding the catalyst, the pressure tubes were placed in a silicon oil bath and stirred using a magnetic stirrer. The reaction was quenched after the desired duration by placing the reactor tube into a beaker filled with ice-water mixture at zero degrees Celsius.

Analysis of the apple juice filtrates

The organic MIBK layer was analysed using a GC8000 gas chromatograph (Interscience) equipped with a capillary column heated at 150 °C connected to a Flame Ionization Detector (FID). To quantify the 5-HMF content a calibration curve was prepared consisting of pure 5-HMF (Alfa Aesar) dissolved as 1.0 mg/mL, 2.5 mg/mL, 5 mg/mL, 10 mg/mL and 20 mg/mL concentrations dissolved in MIBK. The concentration of 5-HMF in the reaction samples was determined via interpolation. Nitrogen was used as the carrier gas. The water layer originating from the apple pomace was analysed using a Waters Alliance HPLC equipped with a 2414 RI detector which was heated to 50 °C. The separation was done using a KS-801 HPLC Column and a Shodex KS-G Guard Column was used. A 0.001 M NaOH (VWR) milliQ water solution was used as the mobile phase which was pumped with a flow rate of 1.0 mL/min. To quantify the components in the water layer calibration curves were prepared for glucose (Merck), sucrose (Merck), fructose (Merck), Levulinic acid (Acros) and 5-HMF (Alfa Aesar) in the 0–300 mg/mL range. Prior to injection the water samples were filtered using a 20 µm PTFE syringe filter. The reaction solutions were quantified by using external calibration. All analysis was within the error limits of ±5%.

The total sugar concentration was calculated by summing up the sugars present in the treated or untreated filtrate liquor as shown in Eq. (1).

$$[Total\ sugar] = [Glucose] + [Fructose] + [Sucrose] \quad (1)$$

Table 1

Composition of the prepared filtrates.

Sample	Filter type	Pore size (µm)	pH	Solid content filtrate (wt. %)	Solid residue filter (wt. %)	Glucose (mg/mL)	Fructose (mg/mL)	Sucrose (mg/mL)	Total sugar (M)	5-HMF (mg/mL)	Yield* (%)	Filtration speed (ml/min)
AS	–	–	3.32	12.9	–	27.4	67.3	9.6	0.55	0	97	–
AS_Diluted	–	–	3.37	5.1	–	12.2	24.8	3.8	0.22	0	97	–
AF_54µm	Fabric	54	3.42	4.3	0.7	11.8	26.4	3.8	0.22	0	88	20
AF_2µm	Paper	2	3.44	4.0	1.0	11.1	24.8	3.6	0.21	0	84	1.7
AF_0.2µm	Ceramic	0.2	3.24	0.0	5.1	12.0	26.0	3.4	0.22	0	79	0.8

* Compared to the initial amount of raw biomass feedstock.

The yield variance (YV) for the glucose, fructose, sucrose and all sugars combined (Total sugar) was defined as the variation in sugar concentration between the fresh filtrate and the filtrates which have been treated or exposed to catalytic evaluation. This was calculated according to formula (2) using glucose as an example.

$$YV_{Glucose} = \left(\frac{[Glucose]_{treated\ filtrate}}{[Glucose]_{initial\ filtrate}} * 100\% \right) - 100\% \quad (2)$$

The 5-HMF yield was calculated based on the initial total sugar concentration as depicted in formula (3).

$$Y_{5-HMF} = \frac{[5-HMF]}{[Total\ sugar]_{initial}} * 100\% \quad (3)$$

The Total sugar conversion in the catalytic evaluation is calculated according to Eq. (4).

$$X_{Total\ sugar} = \frac{[Total\ sugar]_{initial} - [Total\ sugar]_{after\ reaction}}{[Total\ sugar]_{initial}} * 100\% \quad (4)$$

The selectivity of the catalyst to 5-HMF was calculated according to Eq. (5).

$$S_{5-HMF} = \frac{[5-HMF]}{[Total\ sugar]_{initial} - [Total\ sugar]_{after\ reaction}} * 100\% \quad (5)$$

Results

Apple mixture filtration

Table 1 summarizes the properties of the apple slurry (AS) sample after milling the apples and the filtrates obtained after filtration of the AS_diluted sample. Upon milling the apples into a mixture, a small amount (~3%) of material is lost as can be seen by the yield of 97% for the AS sample. Analysis of the solid content for the AS sample reveals a dry solid content of 12.9 wt.%. Analysis of the sugar composition reveals fructose to be the main component (67.3 mg/mL), followed by glucose (27.4 mg/mL), while the mixture contained sucrose in the lowest concentration (9.6 mg/mL). The sugar composition and filtration were similar for the samples before and after filtration. When comparing the amount of solid material present in the filtrates after filtering the AS_Diluted sample differences can be observed. The sample filtrate obtained upon filtration over a fabric filter (AF_54 µm) showed a decrease of ~16 % in comparison to the unfiltered diluted apple slurry. Filtration of AS_Diluted over a paper filter resulted in ~22% solid reduction in the final filtrate (AF_2 µm). The highest filtration efficiency was obtained when the AS_Diluted sample was exposed to filtration over the ceramic filter showing 0 % of solid content in the final AF_0.2 µm filtrate sample. The filtration time increased with smaller pore size of the filter material.

In an attempt to reduce filtration time, the apple slurry after dilution was treated by heat, acid and/or base treatment in order to hydrolyse the cellulose partially into monosaccharides and reduce

Table 2Effect on sugar composition after pre-treatment of the apple slurry followed by filtration over the 0.2 μm filter.

Sample	Temperature (°C)	Duration (min)	Additive	Slurry : HCl ratio (w/w)	pH	YV _{Glucose} [*] (%)	YV _{Fructose} [*] (%)	YV _{Sucrose} [*] (%)	YV _{Total sugar} [*] (%)
AF_0.2 μm **	–	–	–	–	3.22	0	0	0	0
	100	30	–	–	3.22	+28	+6	–87	+5
	100	120	–	–	3.22	+41	+12	–99	+9
	100	240	–	–	3.22	+36	+2	–99	+1
	100	30	HCl	200:1	1.5	+36	+12	–99	+7
	100	30	HCl	100:1	1.5	+40	+13	–92	+9
	100	30	HCl	50:1	1.5	+34	+3	–88	+2

^{*} The yield variance (YV) was calculated according Eq. (2). The concentrations of the various sugars determined for the fresh AF_0.2 μm presented in Table 1 were used as the initial concentrations in the equation to calculate the various YV.

^{**} The fresh AF_0.2 μm filtrate concentrations were taken as the reference for the YV calculations, hence the YV of 0% for this entry.

the solids content of the mixture. The influence of this pre-treatment method was tested on the ceramic filter since this filter was prone to the slowest filtration flux. Filtration testing showed that the flux through the ceramic filter was not affected by the pre-treatment procedure. The sugar content of the final filtrate mixture after pre-treatment and filtration were determined and is summarized in Table 2. The results show an alteration in the sugar composition upon pre-treatment and filtration resulting in a higher total sugar content. The highest sugar content was obtained when using solely heat treatment for 2 h. Similar concentrations were reached at a shorter reaction period of 0.5 h when HCl (1.0 M) was added during heat treatment. No sucrose was observed in the reaction liquor after heat treatment even after addition of HCl. It is likely to assume that the increase in sugar content can be ascribed to the hydrolysis of the β -linkage in the sucrose molecule linking the glucose and fructose moiety. Interestingly, the sucrose concentration is slightly higher for the samples treated with HCl. This can be attributed to depolymerization of cellulose.

A part of the apple juice filtrates was neutralized to pH 7 in order to investigate the effect of pH on the catalytic conversion. In order to neutralize the solution to pH 7, the apple juice filtrates were treated with NaOH and Na_2CO_3 . The pH adjusted filtrates were measured in HPLC and the obtained results are shown in Table 3. The results reveal that treatment of the apple juice with Na_2CO_3 or NaOH did slightly increase the sugar content (~5%) for almost all samples. The non-diluted apple mixture sample AS showed a small decrease in sugar content.

Catalytic evaluation

The prepared apple mixtures and filtrates, both neutralized with NaOH or Na_2CO_3 and not neutralized apple mixtures and filtrates were tested in catalytic experiments using the Amberlyst-15 exchanged for one time with a 1 M SnCl_2 solution as reported earlier [11]. The catalytic evaluation was conducted at 120 °C and 2 h which are the optimal conditions for this catalyst. The results are summarized in Table 4. Blank experiments conducted on the apple mixtures and the filtrates at 120 °C for 2 h without catalyst revealed that no 5-HMF was formed. Heat treatment of the non-diluted AS lead to a strong reduction in the total sugar content. Interestingly, the largest reduction in total sugar content was obtained during the blank experiments for the diluted apple slurry (AS_Diluted). Surprisingly, the AF_2 μm sample showed only a minor reduction in the total sugar content (~6%). The sucrose yield was substantially lower, but is likely converted into fructose and glucose. Observing the yields of the separate sugars reveals that after the blank experiments no sucrose was observed, indicating that heat treatment partially leads to the hydrolysis into fructose and glucose. This also explains a slight increase in the glucose concentration for these samples and coincides with the findings

from the mixture pre-treatment using heating discussed in this paper.

Addition of the Sn-Amberlyst-15 catalyst to the reaction product and exposure to 2 h at 120 °C leads to a strong reduction in the total sugar content to approximately 50% for all samples of the original sugar concentration. After neutralizing the reaction mixtures with NaOH and Na_2CO_3 the sugar conversions were slightly higher compared to the non-neutralized samples. However, the yields to 5-HMF were substantially lower for the diluted apple slurry and the filtrates after neutralization. Interestingly, the activity of the Sn-Amberlyst-15 catalyst was hampered more severe in the apple slurry neutralized using Na_2CO_3 .

Effect of salt addition

The effect of salt addition and the type of cation was tested on the apple juice filtrates on the filtrates prepared with the 54 μm filter since these samples showed the highest selectivity towards 5-HMF. The mixtures were catalytically tested for 2 h at 120 °C and using MIBK as extraction fluid using the same acidic Amberlyst-15 resin exchanged for one time with a 1 M SnCl_2 solution as used previously in this study. The salting out effect has been published before [25,26] to support HMF diffusion towards the MIBK layer increasing the ratio of the HMF in MIBK to the HMF in water, further this ratio is referred to the partition coefficient. By removal of HMF from the water layer, the equilibrium of the tandem reaction can be shifted to HMF production and HMF is removed from the water layer thereby preventing by-product formation.

Table 5 shows the results from the catalytic evaluation. The addition of salts to the reaction mixture lead to a substantially higher conversion of the present sugars in the order $\text{CaCl}_2 > \text{KCl} > \text{NaCl}$. The yield in HMF however varied. The additions of KCl yielded similar amounts of 5-HMF, while the addition of CaCl_2 and NaCl showed lower yields towards 5-HMF. When studying the partition coefficients, a lower partition coefficient was obtained for reaction mixtures using NaCl (0.36) and KCl (0.68) compared to the reaction mixture without salt added (1.08). Addition of CaCl_2 leads to an increased partition coefficient of 1.88.

Discussion

Three types of filters with varying in pore sizes have been evaluated for the separation of apple pomace and apple juice from an apple slurry after cutting them in a food processor and diluting in water to an apple pomace to water ratio of 1.0:1.3. The finest pore (~0.2 μm) filter showed the lowest filtration speeds which are likely due to pore blockage of the filter. A fine layer of solids was observed to be formed supporting this hypothesis. The prefiltered mixture was treated by heating, acid or base addition, but did not influence the filtration speed. The pre-treatment conditions were

Table 3
Composition of the apple slurries and filtrates before and after neutralization.

Sample	Base	pH	Glucose concentration (mg/mL)	Fructose concentration (mg/mL)	Sucrose concentration (mg/mL)	Total sugar concentration (mol/l)	5-HMF concentration (mg/mL)
AS	–	3.32	27.4	67.3	9.6	0.55	0
	NaOH	6.99	27.3	61.8	6.3	0.51	0
	Na ₂ CO ₃	7.00	33.6	65.7	8.0	0.57	0
AS_Diluted	–	3.37	12.2	24.8	3.8	0.22	0
	NaOH	7.00	12.6	26.9	3.4	0.23	0
	Na ₂ CO ₃	7.01	13.7	26.4	3.7	0.23	0
AF_54 μm	–	3.42	11.8	26.4	3.8	0.22	0
	NaOH	6.98	12.4	26.5	3.1	0.23	0
	Na ₂ CO ₃	7.01	13.2	26.7	3.3	0.23	0
AF_2 μm	–	3.44	11.1	24.8	3.6	0.21	0
	NaOH	7.00	12.6	26.3	3.4	0.23	0
	Na ₂ CO ₃	7.00	12.8	25.5	3.6	0.23	0
AF_0.2 μm	–	3.24	12.0	26.0	3.4	0.22	0
	NaOH	7.02	12.2	26.1	3.1	0.22	0
	Na ₂ CO ₃	6.98	12.5	26.3	3.3	0.23	0

Table 4
Results obtained from catalytic batch experiments.

Sample	Catalyst	Neutralizing Base	T (°C)	t (h)	YV _{Glucose} [*] (%)	YV _{Fructose} [*] (%)	YV _{Sucrose} [*] (%)	Y _{5-HMF} [*] (%)	S _{5-HMF} (%)	X _{Total sugar} [*] (%)
AS	–	–	120	2	+7	–28	–88	0	0	21
	1xSn-Amb	–	120	2	+1	–64	–90	12	26	47
	1xSn-Amb	NaOH	120	2	+13	–62	–94	5	11	41
AS_Diluted	–	–	120	2	+48	–46	–90	12	60	18
	1xSn-Amb	–	120	2	–4	–25	–11	0	0	31
	1xSn-Amb	Na ₂ CO ₃	120	2	–3	–81	–88	19	33	57
AF_54 μm	–	–	120	2	–8	–68	–95	12	3	51
	1xSn-Amb	NaOH	120	2	–16	–77	–94	12	13	58
	1xSn-Amb	Na ₂ CO ₃	120	2	–13	–39	–38	0	0	20
AF_2 μm	–	–	120	2	+10	–75	–88	17	33	51
	1xSn-Amb	–	120	2	–3	–62	–95	5	10	46
	1xSn-Amb	NaOH	120	2	–8	–76	–73	6	7	54
AF_0.2 μm	–	–	120	2	+7	–6	–88	0	0	6
	1xSn-Amb	–	120	2	+15	–76	–87	18	36	50
	1xSn-Amb	NaOH	120	2	–3	–66	–97	5	11	49
AF_0.2 μm_HCl	–	–	120	2	–50	–91	–97	7	4	78
	1xSn-Amb	Na ₂ CO ₃	120	2	–1	–11	–88	0	0	11
	1xSn-Amb	–	120	2	+6	–77	–86	11	23	53
AF_0.2 μm_HCl	–	–	120	2	–13	–69	–100	14	25	41
	1xSn-Amb	NaOH	120	2	–18	–67	–81	20	37	47
	1xSn-Amb	Na ₂ CO ₃	120	2	–3	–75	–86	16	32	–49
AF_0.2 μm_HCl	–	–	120	2	–1	–72	–46	18	34	–48
	1xSn-Amb	NaOH	120	2	–1	–72	–46	18	34	–48
	1xSn-Amb	Na ₂ CO ₃	120	2	–1	–72	–46	18	34	–48

^{*} The yield variance (YV) was calculated according Eq. (2). The concentrations of the various sugars determined for the fresh filtrates presented in Table 1 were used as the initial concentrations in the equation to calculate the various YV.

Table 5
The effect of type of salt and salt concentration on the catalytic conversion.

Sample	Salt	Temperature (°C)	Reaction time (h)	YV _{Glucose} [*] (%)	YV _{Fructose} [*] (%)	YV _{Sucrose} [*] (%)	Y _{HMF} (%)	S _{HMF} (%)	X _{Total sugar} (%)	Partition coefficient
AF_54 μm	–	120	2	15	–76	–87	18	36	–50	1.00
	2.0 M NaCl	120	2	–13	–69	–100	11	19	–43	0.36
	2.0 M KCl	120	2	–18	–67	–81	19	31	–37	0.68
	2.0 M CaCl ₂	120	2	–75	–93	–89	12	12	–12	1.88

^{*} The yield variance (YV) was calculated according Eq. (2). The concentrations of the various sugars determined for the fresh AF_54 μm presented in Table 1 were used as the initial concentrations in the equation to calculate the various YV.

chosen in such way that they are applicable for local production. Likely the chosen conditions to pre-treat the apple mixture were too mild to breakdown the particles present in the mixture such as (hemi-)cellulose fibres or proteins blocking the filter. Interestingly, the pre-treatments did however increase the sugar contents of the mixtures. Possibly some poly-saccharides were (partly)hydrolysed resulting in the increase in mono-saccharide concentration. From this there could be potential in processing the filtered solids further to extract more sugars.

The catalytic evaluation revealed that neutralization of the reaction mixtures leads to slightly lower yields of 5-HMF compared to the fresh filtrates. Possibly the lower pH assists in the catalytic conversion of sugars to 5-HMF [27]. Also, the addition of cations can potentially lead to lower 5-HMF yields possibly due to catalyst deactivation. The free cations might exchange to the BAS, lowering the rate of fructose dehydration. Interestingly, the neutralization experiments as well as the addition of salts leads to higher glucose conversion which correlates to findings reported in literature [28].

Comparing our findings to the current literature, our study provides a detailed and structured study of various process parameters which could potentially enable the feasible catalytic production of 5-HMF from sugar rich biomass waste streams. Various process parameters has been shown in previous literature to be advantageous for the catalytic conversion of aqueous solutions containing glucose, fructose or sucrose. However, the effect of these parameters has not been tested when converting a real apple fruit waste. Our findings that the pH adjustment, thermal pre-treatment or salt addition are not beneficial for the catalytic process highly simplifies the new process designs. Furthermore, we show that filtration improves the 5-HMF production, and the use of 54 μm pore filters is sufficient. This finding is crucial for a system design since the wider pore filtering speeds up the filtration process and, likewise the overall conversion speed of the biomass waste.

Conclusions

In this study we investigated the most effective way to pre-treat and convert waste apples into a sugar rich feedstock for the catalytic conversion into 5-HMF using a cheap and easy to prepare Sn exchanged acidic Amberlyst-15 resin. The effect of various approaches for the pre-treatment of real fruit waste has been evaluated for the catalytic conversion to 5-HMF. These new insights will allow the development of novel small scale industrial processes for the localised production of 5-HMF. After converting the apples into it a mixture by milling and dilution with water the filtrates the effect of filter fraction was investigated by varying the pore size (0.2 μm , 2 μm and 54 μm). It was found that wider pore filtration obtained the highest filtration speed without the need for additional treatment steps compared to smaller pore sized filters. Catalytic evaluation revealed that using filtrates treated over filters with a pore size of 2 μm and 54 μm provided the highest HMF yields and selectivities. Catalytic conversion of the diluted apple slurry resulted in similar HMF yields. Dilution neutralization using Na_2CO_3 and NaOH lead to a slightly lower yield of 5-HMF during the catalytic upgrading of the obtained apple filtrate juices. Also, the addition of NaCl, KCl and CaCl_2 salts was shown to result in lower 5-HMF yields during catalytic conversion. From our study it is shown that the simple milling the apple biomass into a mixture followed by filtration (route A in Fig. 1) using a 54 μm filter

provides the best way to provide a sugar rich feedstock stream from agricultural apple waste for the catalytic conversion into 5-HMF at low temperatures (120 °C).

Conflict of interests

There are none financial interests/personal relationships whatsoever which may be considered as potential competing interests.

References

- [1] R.-J. van Putten, J.C. van der Waal, E. de Jong, C.B. Rasrenda, H.J. Heeres, J.G. de Vries, *Chem. Rev.* 113 (2013) 1499.
- [2] G.P. Perez, A. Mukherjee, M.-J. Dumont, *J. Ind. Eng. Chem.* 70 (2019) 1.
- [3] M. Moliner, Y. Román-Leshkov, M.E. Davis, *Proc. Natl. Acad. Sci. U. S. A.* 107 (2010) 8954.
- [4] R. Oozeerally, S.D.K. Ramkhelawan, D.L. Burnett, C.H.L. Tempelman, V. Degirmenci, *Catalysts* 9 (2019) 812.
- [5] F. Menegazzo, E. Ghedini, M. Signoretto, *Molecules* 23 (2018) 1.
- [6] V. Degirmenci, E.J.M. Hensen, *Environ. Prog. Sustain. Energy* 33 (2014) 657.
- [7] A. Sarwono, Z. Man, C.D. Wilfred, *J. Ind. Eng. Chem.* 69 (2019) 171.
- [8] Y. Román-Leshkov, M. Moliner, J.A. Labinger, M.E. Davis, *Angew. Chem.* 49 (2010).
- [9] E.A. Pidko, V. Degirmenci, E.J.M. Hensen, *Chemcatchem* 4 (2012) 1263.
- [10] A.A. Marianou, C.M. Michailof, A. Pineda, E.F. Iliopoulou, K.S. Triantafyllidis, A. A. Lappas, *Appl. Catal. A* 555 (2018) 75.
- [11] C. Tempelman, U. Jacobs, T. Hut, E. Pereira de Pina, M. van Munster, N. Chersakov, V. Degirmenci, *Appl. Catal. A* 588 (2019) 117267.
- [12] M.C. Edwards, J. Doran-Peterson, *Appl. Microbiol. Biotechnol.* 95 (2012) 565.
- [13] R. Ito, H. Miyafuji, Y. Miyazaki, T. Kawai, *J. Wood Sci.* 62 (2016) 349.
- [14] J.N. Chheda, Y. Román-Leshkov, J.A. Dumesic, *Green Chem.* 9 (2007) 342.
- [15] N. Sweygens, N. Alewaters, R. Dewil, L. Appels, *Sci. Rep.* 8 (2018) 7719.
- [16] A.B. Moldes, J.L. Alonso, J.C. Parajó, *J. Biosci. Bioeng.* 87 (1999) 787.
- [17] S.H. Krishna, T.J. Reddy, G.V. Chowdary, *Biores. Technol.* 77 (2001) 193.
- [18] C.O. Tuck, E. Pérez, I.T. Horváth, R.A. Sheldon, M. Poliakoff, *Science* 337 (2012) 695.
- [19] F. Cherubini, *Energy Convers. Manage.* 51 (2010) 1412.
- [20] B. Gullón, E. Falque, J.L. Alonso, J.C. Parajó, *Food Technol. Biotechnol.* 45 (2007) 426.
- [21] G.S. Dhillon, S. Kaur, S.K. Brar, *Renew. Sustain. Energy Rev.* 27 (2013) 789.
- [22] N. Mahato, K. Sharma, M. Sinha, M.H. Cho, *J. Funct. Foods* 40 (2018) 307.
- [23] T. Kläusli, *Green Process Synth.* 3 (2014) 235.
- [24] I. Parmar, H.P. Vasantha Rupasinghe, *Bioresour. Technol.* 124 (2012) 433.
- [25] Y. Román-Leshkov, J.A. Dumesic, *Top. Catal.* 52 (2009) 297.
- [26] S. Altway, S.C. Pujar, A.B. de Haan, *J. Chem. Thermodyn.* 132 (2019) 257.
- [27] P. Körner, D. Jung, A. Kruse, *ChemistryOpen* 8 (2019) 1121.
- [28] M. Kammoun, T. Istasse, H. Ayeb, N. Rassaa, T. Bettaieb, A. Richel, *Front. Chem.* 7 (2019) 1.