Catalytic Pyrolysis of Plastics over Maghemite-Impregnated Mesocellular Foam using Induction Heating

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Pyrolysis is a key technology that converts unrecyclable end-of-life plastics into value-added products. Nevertheless, the high energy consumption during plastic pyrolysis limits the economic feasibility of a scaled-up process. Development of an energy-efficient plastic pyrolysis process is necessary to realise its full potential in the circular economy. Catalysts derived from mesocellular foam possess high acidity and mesoporosity, and exhibit high catalytic activity in chemical reactions. Application of such catalyst in plastic pyrolysis has never been reported. This work presents the catalytic pyrolysis of low- and high-density polyethylene and polypropylene over maghemite-impregnated mesocellular foam (Fe@AlMCF). Fe@AlMCF has a BET surface area of 629.8 m^2/g and a strong Brønsted acidity (677 µmol/g_{cat}). The catalyst contains pentagonal and hexagonal packed mesostructure. Induction heating resulted in a rapid increase in reactor temperature (at 65 °C /min) and complete plastics conversion within 10 min. Catalytic pyrolysis produced gas products rich in C3 compounds. The liquid products were rich in alkenes (69.7-71.3 %) and alkanes, followed by aromatics (10.4-12.8 %). These observations indicate that the highly acidic Fe@AlMCF catalysed hydrocarbon aromatization within a short reaction time. Thermal analysis of the spent catalysts revealed considerably high coke yields (5.78 - 6.03 %), as the higher acidity of the original catalyst promoted coke precursor formation. Based on the research findings, induction heating can rapidly and effectively convert plastics into hydrocarbon feedstocks, and Fe@AlMCF is a valuable catalyst for plastic pyrolysis.

1. Introduction

Human civilisation generates a large amount of plastic waste which threatens the environment human well-being. The global plastic waste generation is forecasted to increase from 225 million metric tons (2016) to 420 x 10^6 t (2040) (Palardy, 2022). Pyrolysis is an important technology that retains the material value of plastics in the circular economy. Pyrolysis is the high-temperature decomposition of complex materials (at 400-800 °C) in an inert environment. Such process converts plastic waste into value-added products, including liquid fuels, chemical feedstock and carbon nanomaterials (Wong et al., 2022). Plastic pyrolysis technology is an essential component in the SuSChem Strategic Innovation and Research Agenda, which requires the alignment of all actors in the innovation ecosystem (SusChem, 2020). There are numerous publications in the literature that describe the effectiveness of pyrolysis in plastic waste conversion to liquid products (in the gasoline and diesel range) and gas products (especially hydrogen and light hydrocarbon molecules) (Armenise et al., 2021). The product yields and compositions depend mainly on the reactor system and process conditions used. The use of acidic and porous catalysts, especially zeolites, effectively reduces the activation energy of plastic chain-

scission while leading to desirable product compositions (Suarez-Torielloa et al., 2021). Due to the high acidity and mesoporosity, aluminum-containing mesocellular silica foam (AlMCF) demonstrates excellent catalytic activity in alcohol esterification (Liu et al., 2008) and dibenzothiophene hydrodesulfurization (Song et al., 2017). The potential of MCF-derived catalysts in plastic pyrolysis has not been investigated. The maghemite impregnation in the catalyst enables easy catalyst recovery from the reaction residue, simply by using magnetic force.

Several important issues limit the potential of large-scale plastic waste pyrolysis. As plastic pyrolysis is an endothermic reaction, the significant energy cost in the scaled-up process reduces the cost-competitiveness of the pyrolysis oil against the petroleum-based oil, and results in high carbon emissions. Most research teams have utilised resistive heating in plastic pyrolysis, which is associated with slow heating and cooling rates and low energy efficiency of the waste valorisation process. This shortcoming is responsible for the high energy consumption and aforementioned low economic viability of large-scale plastic waste recycling. A potential solution to this challenge is the replacement of resistive heating with induction heating, which is a non-contact technique involving the induction of eddy current in a ferromagnetic metal in an alternating magnetic field. The eddy current generates the Joule heating effect, which leads to rapid heat generation on the metal surface. As most pyrolysis reactors are made of stainless steel (a good susceptor in an alternating magnetic field), the application of induction heating in pyrolysis could be a key innovative solution to achieve higher energy efficiency and economic feasibility for large-scale applications. According to Sosa Sabogal et al. (2021), the reaction zone of a stainless-steel reactor can be heated to 800 °C within 2.5 - 5 min. Tsai et al. (2007) showed that rice husk pyrolysis via induction heating of the reactor took only 1 – 8 min, which is faster than the (conventional) biomass pyrolysis using resistive heating of the reactor (20-60 min (Boubacar et al., 2020)). Induction heating of reactor wall has been applied in solid waste (Sosa Sabogal et al., 2021) and lignocellulosic waste (Muley et al., 2015) pyrolysis, no study was dedicated to plastic waste valorisation.

To fill this knowledge gap, an exploratory study was performed to investigate catalytic pyrolysis of neat plastics over a novel catalyst, maghemite impregnated in maghemite-impregnated mesocellular foam (Fe@AlMCF), in a self-fabricated stainless-steel reactor using induction heating. Specifically, low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene (PP) pellets were pyrolyzed to determine the yield and compositions of gas and liquid products. The catalyst coking behaviour was also studied.

2. Materials and Methods

This section presents the information of the plastics and catalysts used, together with the characterization methods and product analysis methods in this study.

2.1 Materials

Virgin LDPE, HDPE and PP pellets were obtained from a Spanish petrochemical company and were used as received. Synthesis of magnetic-Fe@AlMCF was carried out in two steps. Firstly, the magnetic nanoparticle of maghemite (γ-Fe_2O_3) was prepared following the methodology reported by Lefebure et al. (2011). Maghemite was synthesized by alkalinisation of aqueous mixtures of ferric chloride and ferrous chloride (0.5 M $FeCl_3$ and 2.3 M $FeCl_2$) at room temperature in a molar solution of ammonia. The typical concentration of iron species in the final solution was 1.4 M. The mesocellular silica-alumina foam synthesis was performed by varying the method described by Daoura et al. (2018), which incorporated aluminium isopropoxide as the Al-source and nitric acid as solvent. The typical process involves preparing two solutions. Solution "A" was prepared as follows: 4 g of the triblock copolymer ($EO_{20}PO_{70}EO_{20}$, Pluronic P123) was dissolved in a solution of HNO_3 (150 mL, pH=1) at 40 °C. Next, 4 g of TMB was added dropwise into the mixture under strong stirring to obtain a microemulsion. Solution "B" consisted of 6.4 mL tetramethylorthosilicate (TMOS) and 0.8 g of Al-isopropoxide dissolved into 10 mL of HNO_3 (pH=1), at room temperature. The solutions A and B were subsequently mixed at 40 ºC for 24 h and finally subjected to hydrothermal treatment at 100 °C for 24 h. Next, 48 mg of NH_4F and 1 mL of maghemite solution previously prepared was incorporated. The suspension was then filtered with a neodymium magnet and the recovered solid was washed, dried, and calcined under airflow at 550 °C for 5 h (heating rate 1 °C/min). The non-dark-brown solution after washing was collected, indicating maghemite was well-anchored on the AlMCF. The final calcined sample was labelled Fe@AlMCF. The Si/Al ratio of the catalyst was 10.4 (similar to typical ZSM-5 zeolites) with a Fe content (wt%) of 3.9. The textural properties of the catalyst were characterized based on the nitrogen adsorption-desorption isotherm produced by a Micromeritics Gemini 2360 instrument (USA) at -196 °C. The amount and strengths of catalysts' acidic sites were characterized using temperature-programmed decomposition of n-propylamine in a DSC-TGA thermal analyser (model: SDT Q600, TA Instruments, USA). The morphology of Fe@AlMCF was analysed using Scanning Electron Microscopy (SEM, Hitachi SU3800, Japan) and Transmission Electron Microscopy (TEM, JEOL 1011, Japan).

2.2 Catalytic pyrolysis of plastics

A fixed bed reactor system was used for plastic pyrolysis by induction heating. The reactor also acted as a susceptor of electromagnetic field produced by a 3-turn copper coil (length: 9.8 cm, inner diameter: 3.0 cm) connected to an induction heater (Easyheat system, Ambrell, UK) with an output power of 1.2 kW. A stainless-steel cold trap connected to the (bottom) reactor outlet was maintained at 2 °C to collect the condensable reaction products. The non-condensable gases were collected in a water column after the cold trap. In this exploratory study, 0.25 g of plastic pellets (LDPE, HDPE, or PP), together with 0.05 g of Fe@AlMCF, were placed on a quartz wool layer (0.20 g) in the reactor. Before the pyrolysis process, the reactor system was purged with nitrogen gas (120 mL/min) for 10 min to ensure an inert environment. Next, the nitrogen gas flow was turned off. The induction heater was turned on for 30 min to allow reactor heating. After 30 min, the induction heater was turned off, and the reactor was allowed to cool to room temperature. The condensed product was extracted with 3 mL of dichloromethane before being weighed and analysed. All the pyrolysis experiments were performed in duplicates. The amount of coke formed on the catalyst was characterized using the temperature-programmed oxidation (TPO) technique (Xu et al., 2020). The light hydrocarbon compounds in the gas products were analysed using a Shimadzu 2010 GC (Japan) equipped with an FID column (Fekhar et al., 2019), while the chemical composition of the liquid products was analysed using a Thermo Scientific™ Q Exactive™ GC Orbitrap™ GC-MS/MS System (USA) (Ding et al., 2019).

The heating power of the induction heater was selected to ensure the complete conversion of the plastic pellets in all the experiments. As a result, no plastic remained in the reactor after pyrolysis reactions. The masses of the liquid products after pyrolysis were weighed after extraction with dichloromethane. The gas yield in this study is expressed in the total volume of the gas product per mass unit of plastic pellet, expressed in mL/g. The amount of coke formed on the catalyst was characterized using the TGA/TPO technique. For each test, 10 mg of the spent catalyst was heated to 800 °C using a thermo-gravimetric analyser (TGA/DSC STAR system, METTLER TOLEDO, USA) at a heating rate of 15 °C min⁻¹, followed by a hold for 10 min at 800 °C, with an airflow rate of 100 mL/min. The analysis result was used to calculate the total mass of coke formed on the catalyst. The coke yield was calculated using Eq (1):

$$Coke\ yield, x_c(\%) = \frac{m_c}{m_p} \times 100 \qquad (1)$$

where m_c (g) is the total coke mass, m_c (g) is the mass of plastic pellets used in the experiment.

3. Results and Discussions

3.1 Catalyst Characterizations

Figure 1a displays the nitrogen adsorption/desorption curve for Fe@AlMCF consisting of types II and IV(a) isotherms. Rapid adsorption of nitrogen molecules is observed at $0 \leq P/Po \leq 0.02$ due to the single-layer adsorption in the mesopores and micropore filling. This is followed by capillary condensation at $P/Po \approx 0.44$.
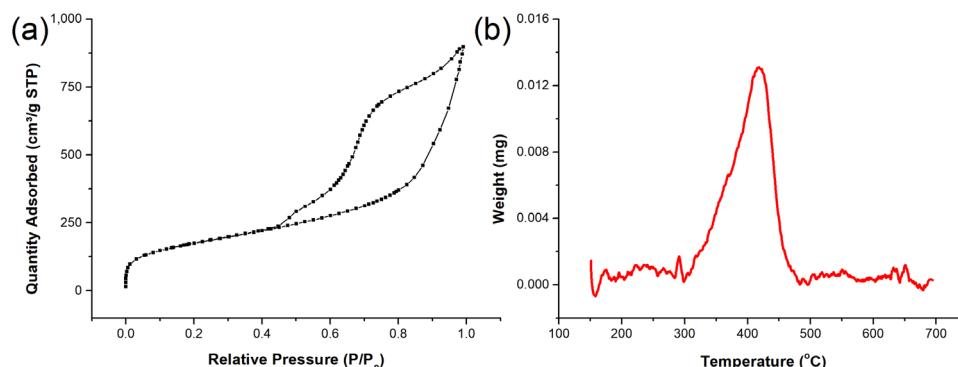

Figure 1: (a) Nitrogen adsorption-desorption isotherms and (b) temperature-programmed decomposition of n-propylamine plot for Fe@AlMCF.

The absence of adsorption saturation signifies the presence of macropores in the catalyst particles. An H4-type hysteresis loop for such a catalyst indicates a mixture of micro- and meso-porosity. A similar isotherm was observed for Ni/γ-Al₂O₃ synthesized by Xu et al. (2020). The BET surface area of Fe@AlMCF is 629.8 m²/g. Figure 1b shows a single peak for n-propylamine decomposition at ≈ 425 °C, indicating a small number of strong Brønsted acidic sites (677 µmol/g$_{cat}$), which catalyses n-propylamine decomposition at a comparatively low temperature. The SEM and TEM images in Figure 2 show that the mesoporous foam has a heterogeneous

pentagonal and hexagonal packed mesostructure, typical for a non-ordered material. The particle size distribution measured by TEM of 300 particles shows monodispersed diameter distribution cantered at 8-10 nm (not shown in this paper).
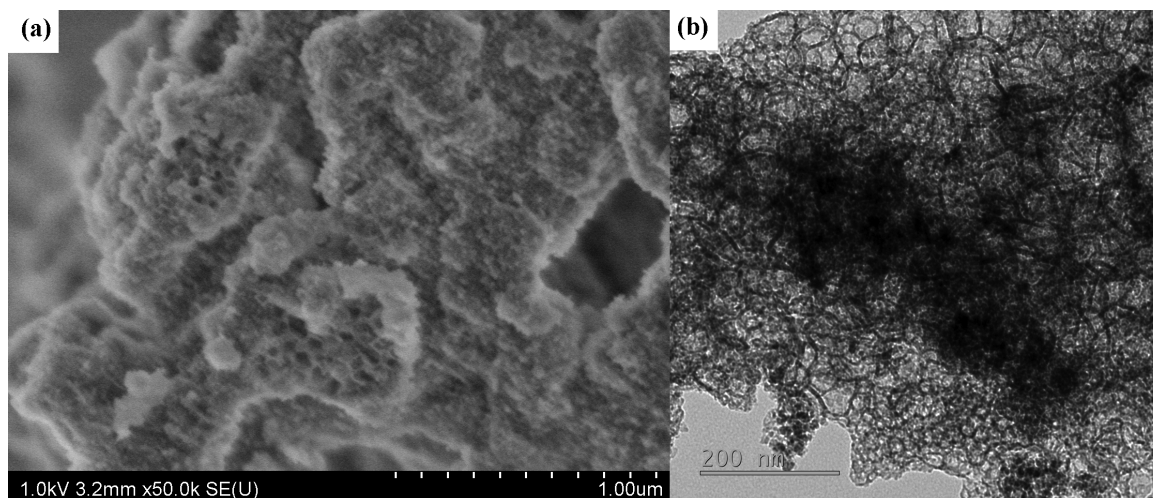

Figure 2: (a) SEM and (b) TEM images of Fe@AlMCF.

3.2 Catalytic pyrolysis of plastics over Fe@AlMCF

The induction heating of the stainless steel reactor raised its temperature to 650 °C within 10 min. As shown in Figure 3a, rapid gas product evolutions were observed in the first 10 min for all the plastic pyrolysis. For PP, a plateau was reached after 15 min, as all the volatile products produced during pyrolysis exited the reactor. Nevertheless, the reaction intermediates formed from LDPE and HDPE continued to undergo secondary reactions, resulting in increased amounts of gas products. Considering the use of 0.25 g of plastics in each experimental run, the amount of gas products produced in catalytic pyrolysis over Fe@AlMCF were 404 mL/g (HDPE), 400 mL/g (LDPE), and 352 mL/g (PP). This observation indicates that PP is less susceptible to the catalytic effects of Fe@AlMCF compared to HDPE and LDPE, as the bulky structure of PP polymer chains hinders effective contacts with the catalyst acidic sites.
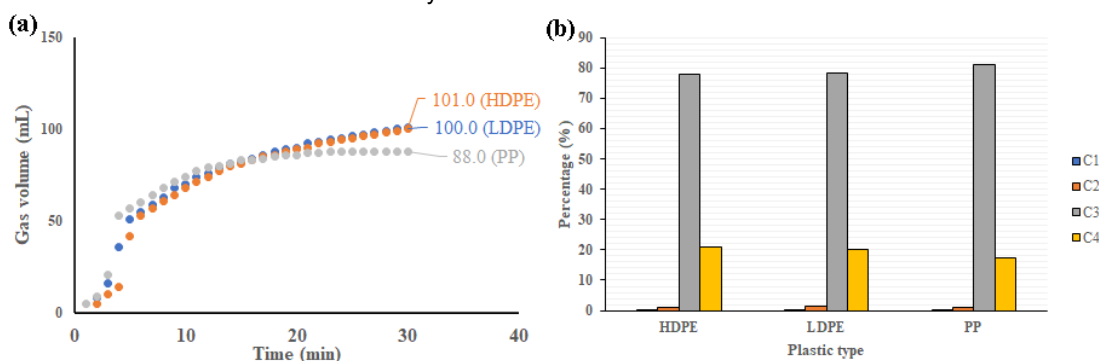

Figure 3: (a) Evolution rates and (b) compositions and gas products from catalytic pyrolysis of plastics over Fe@AlMCF.

The gas products from catalytic pyrolysis of HDPE, LDPE and PP were rich in C3 compounds (propane and propene), which was also observed by Jaafar et al. (2022) in catalytic pyrolysis of plastics for 20 minutes. Such observation indicates extensive cracking of polymer chains on the strong acidic sites of the catalysts at high reaction temperature. In Jaafar et al. (2022)'s work, C2 compounds (ethane and ethene) were the next major group of compounds, while in this study, C4 compounds were the next major group of compounds. Such difference indicates that a longer reaction time is needed to promote the cracking of C4 compounds into smaller hydrocarbon molecules.

Catalytic pyrolysis of HDPE over Fe@AlMCF produced liquid products that contain C5-C31 compounds. This is attributed to the high surface area and abundant Brønsted acidic sites on the catalyst. The liquid products from LDPE and PP also produced similar chromatograms. Catalytic pyrolysis over Fe@AlMCF produced a significant amount of alkenes (69.7-71.3 %) and alkanes (16.4-18.8 %) in the liquid products. A high amount of aromatic

compounds (10.4-12.8 %), including naphthalene, were also observed (Table 1). The roles of Brønsted sites in Fe@AlMCF were weaker than whose on zeolitic catalysts, as reported in the literature (Hasan et al., 2022). These observations could possibly indicate that abundance of the strong acidic sites play a more important role than the BET-surface area and weak acidic sites in the aromatization of plastic pyrolysis intermediates. The effects of plastic-type seemed to exert minor influence on the liquid product distribution in this case.

Table 1: Composition of liquid products from catalytic pyrolysis powered by induction heating.

	Alkanes (C7-C40)				Alkenes (~C7- ~C40)	Aromatic compounds								
	C7-C9	C9-C19	C19-C40	Total		C6	C7	C8	C9	C10	C11	C12	Naph-thalene (C10)	Total
HDPE	1.14	8.68	8.42	18.25	71.34	0.32	0.72	1.24	2.53	3.35	0.53	0.68	1.04	10.41
LDPE	1.28	9.25	5.91	16.43	70.72	0.65	0.97	1.42	2.91	3.86	0.73	0.84	1.46	12.84
PP	0.93	10.58	7.28	18.79	69.72	0.14	0.57	0.99	2.47	4.16	0.81	0.94	1.41	11.49

According to Figure 4, all the spent catalyst samples experienced slight mass reduction from 50 °C to 400 °C, as the carbon species that loosely attach to the catalyst surface was burnt off. Significant mass decrease of the samples in 400 – 625 °C are attributed to the oxidation of polyaromatic coke in the mesopore system of the catalyst. All the derivative thermogravimetric (DTG) curves exhibit the same distinctive peak at ~565 °C, indicating the same chemical structure for the coke formed from the pyrolyzed plastics. The coke yields are 6.03 % (HDPE), 5.83 % (LDPE) and 5.78 % (PP). The results are higher than coke formation/yields observed in zeolitic catalysts (Wang et al., 2019), possibly due to the unique textural properties of the catalysts which favours coke formation. Further investigations on the coke formation will be carried out to reveal the effects of Fe on the plastic pyrolysis behaviour.
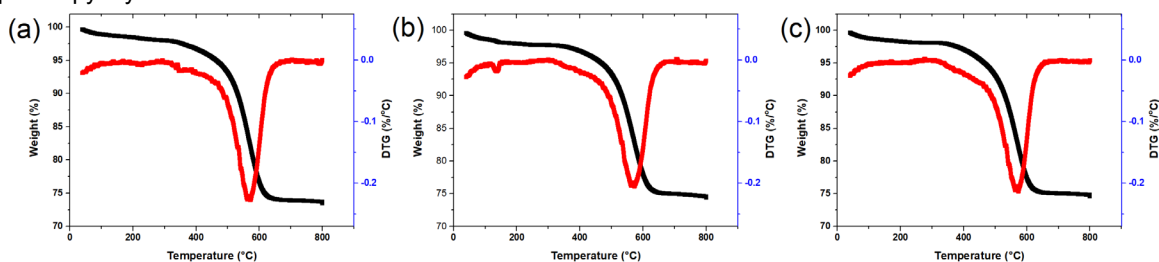

Figure 4: DTG curves for spent catalysts after catalytic pyrolysis of (a) HDPE, (b) LDPE and (c) PP.

4. Conclusions

The Fe@AlMCF synthesized in this study is characterized by a high surface area (629.8 m^2/g) and moderate Bronsted acidic sites (677 µmol/g_{cat}). The morphology of the catalyst shows a broad distribution of pore size characteristic of mesocellular foams, while the nanoparticles of maghemite deposited show homogeneous size centred at 8-10 nm. The reactor temperature could be increased from room temperature to 650 °C within 15 min. The catalytic pyrolysis of HDPE, LDPE, and PP over Fe@AlMCF produced significant hydrocarbon gases (352-404 mL/g), which are rich in C3 compounds as well as liquid products rich in alkanes and alkenes with carbon numbers in the range of C5-C31. The catalytic property of Fe@AlMCF is related to the high surface area, while the acid strength of the catalyst is small to induce significant aromatization of plastic pyrolysis products. High coke yields are observed for all the plastics tested, and more studies are needed to clarify such ideas further. In conclusion, the findings reveal that Fe@AlMCF can be used to pyrolyze plastics into valuable hydrocarbon compounds. The effect of Fe impregnation on the yields and compositions of pyrolysis products requires further examination. Future studies will be carried out to investigate the effects of reaction parameters (induction heater power, catalyst/plastic ratio, reaction time etc) on the plastic pyrolysis performance, and the energy efficiency of the plastic pyrolysis powered by induction heating.

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