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Catalytic pyrolysis of waste plastics using staged catalysis for production of gasoline range hydrocarbon oils

Devy K. Ratnasari, Mohamad A. Nahil, Paul T. Williams*

School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK

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ABSTRACT

The two-stage pyrolysis-catalysis of high density polyethylene has been investigated with pyrolysis of the plastic in the first stage followed by catalysis of the evolved hydrocarbon pyrolysis gases in the second stage using solid acid catalysts to produce gasoline range hydrocarbon oil (C_8–C_{12}). The catalytic process involved staged catalysis, where a mesoporous catalyst was layered on top of a microporous catalyst with the aim of maximising the conversion of the waste plastic to gasoline range hydrocarbons. The catalysts used were mesoporous MCM-41 followed by microporous ZSM-5, and different MCM-41:zeolite ZSM-5 catalyst ratios were investigated. The MCM-41 and zeolite ZSM-5 were also used alone for comparison. The results showed that using the staged catalysis a high yield of oil product (83.15 wt.%) was obtained from high density polyethylene at a MCM-41:ZSM-5 ratio of 1:1 in the staged pyrolysis-catalysis process. The main gases produced were C_2 (mainly ethene), C_3 (mainly propene), and C_4 (mainly butene and butadiene) gases. In addition, the oil product was highly aromatic (95.85 wt.% of oil) consisting of 97.72 wt.% of gasoline range hydrocarbons.

In addition, pyrolysis-staged catalysis using a 1:1 ratio of MCM-41: zeolite ZSM-5 was investigated for the pyrolysis–catalysis of several real-world waste plastic samples from various industrial sectors. The real world samples were, agricultural waste plastics, building reconstruction plastics, mineral water container plastics and household food packaging waste plastics. The results showed that effective conversion of the real-world waste plastics could be achieved with significant concentrations of gasoline range hydrocarbons obtained.

1. Introduction

Plastics are high demand materials, employed in a wide range of applications, from household packaging, agricultural, automotive, to building construction, due to their lightweight characteristics, high chemical stability and low degradability [1]. Current worldwide production of plastics is around 300 million tonnes/year, with 57 million tonnes/year produced in the European Union [2]. Inevitably, much of the plastic will end up in the waste stream and in the EU more than 25 million tonnes of waste plastics are generated each year.

The current process routes for plastic waste management in the EU are ~26% recycling, ~35% used for energy recovery (mainly incineration) and ~38% disposed to landfill [3]. There is also significant export of waste plastics, with a reported 3.4 million tonnes of waste plastic exported out of the EU each year [4]. The process options for recycling waste plastics in the EU are dominated by mechanical recycling which involves for example, sorting, shredding, washing drying and pelletising of the plastic producing a recyclate material. However, there is growing interest in the pyrolysis of waste plastics, where the plastic is thermally degraded at moderate temperature (~500 °C) in the absence of air to produce shorter molecular chains and low molecular weight molecules to produce an oil for potential use as a liquid fuel as reported in several recent reviews [5–8].

To further develop the plastics pyrolysis process, catalysts have been used together with pyrolysis to produce a higher quality liquid fuel which can be used as a premium grade fuel in transport engine systems. Catalysts can play a critical role in the thermochemical processing of waste plastics in terms of promoting targeted reactions, reducing reaction temperature and improving process system efficiency [9]. The most commonly investigated catalysts are solid acid catalysts for example, zeolite ZSM-5, Y-zeolite and MCM-41. Catalytic reactions of the hydrocarbon pyrolysis products produced during the pyrolysis of the waste plastics on solid acid cat-

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* Corresponding author.
E-mail address: p.t.williams@leeds.ac.uk (P.T. Williams).

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alysts include, cracking, isomerisation, oligomerisation, cyclisation and aromatisation reactions [9].

Serrano et al. [9] have reviewed the use of solid acid catalysts for the catalytic pyrolysis of waste plastics (polyalkenes) for the production of fuels and chemicals. They report that the evolved hydrocarbons from the pyrolysis, thermal cracking of the plastic polyalkene (e.g. high density polyethylene) produces a wide distribution of hydrocarbons from C_1–C_{60}. Such a wide range of hydrocarbons limits the size of the molecules which can enter a narrow pore structure catalyst. MCM-41 is an ordered solid acid catalyst with a mesoporous pore structure (1.5–30.0 nm pore size range) whereas zeolite catalysts such as zeolite ZSM-5 and Y- zeolite are microporous (0.4–1.0 nm pore size range) solid acid catalyst with defined ring structures [9]. Therefore, the use of microporous zeolite catalysts limits the range of higher molecular weight hydrocarbons derived from plastics pyrolysis that can enter the pores of the catalyst for reaction. Escola et al. [10] and Serrano et al. [9] have proposed the combined use of the microporous and mesoporous properties of catalysts in a hierarchical catalyst structure to maximise the conversion of the plastics pyrolysis products to lower molecular weight hydrocarbon fuels and chemicals. It should also be noted that the acidity of the catalyst plays a major part in the activity of the catalyst for the conversion of the plastics pyrolysis gases, higher catalyst acidity resulting in higher catalytic activity. Zeolite ZSM-5 and MCM-41 are aluminosilicates where the silica:alumina ratio can be manipulated to produce Si:Al ratios where different amounts of Al replace Si in the crystal structure, thereby for example, producing lower Si:Al ratios which have higher surface acidity and thereby increased catalyst activity.

There have been several studies in the literature reporting the catalytic performance of microporous zeolites such as ZSM-5 and Y-zeolite and mesoporous MCM-41 aluminosilicate catalysts for the catalytic pyrolysis of waste plastics. Uemichi, et al. [11] reported on the catalytic pyrolysis of polyethylene with a HZSM-5 catalyst and showed that the catalyst promoted the formation of gasoline range hydrocarbon fractions comprised of isoalkanes and aromatic compounds from the degradation of polyethylene in a fixed-bed flow reactor system at 526 °C pyrolysis temperature and 450 °C catalyst temperature. The coke deposition in the pores of MCM-41 was less than it in the pores of HY zeolite. When HY zeolite catalyst was introduced for the catalytic degradation of polyethylene, a steep decrease of oil products occurred and the pores of the HY zeolite were blocked by coke formation [11]. Gaca et al. [12] reported that modified MCM-41 and HZSM-5 were able to decrease the degradation temperature of HDPE as well as affect the distribution of the formed products from the cracking process. The liquid products were mostly distributed in gasoline range fractions (C_6–C_{12}) and comprised mainly aliphatic hydrocarbons (alkanes and alkenes). On the other hand, the degradation over HZSM-5 achieved light hydrocarbons (C_3–C_4) of 50 wt.% and were dominated by aromatic compounds [12].

Lin et al. [13] used a fluidised bed reactor to study the catalytic cracking of high density polyethylene with several different catalysts, HZSM-5, SiO_2–Al_2O_3 and MCM-41, and a mixture of MCM-41/HZSM-5 and SiO_2–Al_2O_3/HZSM-5. The HZSM-5 catalyst produced a lighter range of hydrocarbons. Also when the HZSM-5 was mixed with the MCM-41 or SiO_2–Al_2O_3 catalysts less gas with more gasoline range hydrocarbons were produced. The MCM-41 catalyst with larger mesopores and the SiO_2–Al_2O_3 catalyst with weaker acidic sites produced more alkenes and the broadest C_3–C_7 hydrocarbon range. However, the MCM-41 and SiO_2–Al_2O_3 catalysts produced higher formation of catalyst coke.

Aguado et al. [14] used a two-stage, pyrolysis-catalysis reactor for processing polyethylene using zeolite HZSM-5 and MCM-41 catalysts at temperatures between 425 and 475 °C. In the absence of catalyst the product oil (75 wt.%) consisted of alkanes and alkenes, but with the HZSM-5 catalyst, oil yield decreased and gas yield increased to 73.5 wt.%. The oil consisting of aromatic and branched aliphatic compounds with a carbon number range from C_5–C_{12}. Using the mesostructured MCM-41 catalyst produced a higher yield of oil, 34–42 wt.%, depending on catalyst temperature, and a correspondingly lower yield of gas (54–58 wt.%). The aromatic content of the product oils was lower than that produced with the HZSM-5 catalyst, which was attributed to its lower catalytic acidity.

The main objective of much of the published research into the catalytic pyrolysis of waste plastics is to produce a high quality fuel oil with high yield of gasoline range hydrocarbons. Gasoline range hydrocarbons are the hydrocarbons in the range of C_5–C_{12} with low concentrations of the C_{13+} fraction. Research octane number (RON) of more than 90 with low aromatic contents is also required. The RON is a rating of the fuels resistance to knocking or pre-ignition under compression. Wagner et al. [15] noted the current requirements for gasoline in the EU are minimum Research Octane Number (RON) of 95, with maximum alkenes content of 18% v/v, aromatics of 35% v/v, and benzene 1% v/v [15]. Buekens and Huang [16] have detailed the parameters of gasoline-range hydrocarbons. Gasoline quality is usually measured in terms of volatility and octane number of the hydrocarbons. Suitable hydrocarbons in order to obtain adequate volatility for smooth operation of spark ignition engines are in the C_5–C_8 range; some C_9 and above may be added according to climate and season. In addition, fuels with a higher octane number are preferred [16].

This paper reports on the catalytic pyrolysis of waste plastic in the form of high density polyethylene in a two-stage pyrolysis-catalysis system. Pyrolysis of the plastic took place in the first reactor and catalysis using solid acid catalysts in the second stage. The influence of using MCM-41, and zeolite ZSM-5 catalysts on the yield and composition of the derived gases and oils was investigated. In addition, the influence of staging a layered mixture of the MCM-41 with its mesoporous structure followed by zeolite ZSM-5 on the composition of the oils and gases was also investigated. The aim of the staged catalysis was to catalytically crack the higher molecular weight hydrocarbons produced from pyrolysis of the HDPE to lower molecular weight hydrocarbons over the MCM-41 catalyst which could then more easily enter the microporous structure of the zeolite ZSM-5 catalyst.

2. Material and methods

2.1. Materials

High density polyethylene (5 mm spheres) was supplied from Good Fellow Ltd., Cambridge, United Kingdom and used without further treatment. Real-world waste plastic samples were obtained from various industrial sectors and were investigated using pyrolysis-staged catalysis to determine the yield of gasoline range hydrocarbons. The real world samples were, agricultural waste plastics (AW), building reconstruction plastics (BR), mineral water container plastics (MWC), household food packaging waste plastics (HFP), all as flaked samples with a sample size of ∼5 mm. Catalysts (∼1–2 mm spheres) in the form of zeolite ZSM-5 and MCM-41 were obtained from Nankai University Catalyst Plant, China. Table 1 shows the properties of the catalysts.

2.2. Experimental reactor

The pyrolysis-catalysis experimental reactor system consisted of a two-stage fixed bed reactor with oil condensers and gas collection sample bag (Fig. 1). Serrano et al. [9] has suggested that the two-stage thermal cracking followed by catalytic cracking system has many advantages in terms of optimising the production

Table 1
Properties of the Catalysts used.

Catalyst	Si:Al ratio	BET Surface Area ($m^2 g^{-1}$)	Pore Volume ($cm^3 g^{-1}$)		Average Pore Width (nm)
			Micropore	Mesopore	
ZSM-5	20	266	0.23	0.12	5.2
MCM-41	4	799	0.38	0.33	3.95

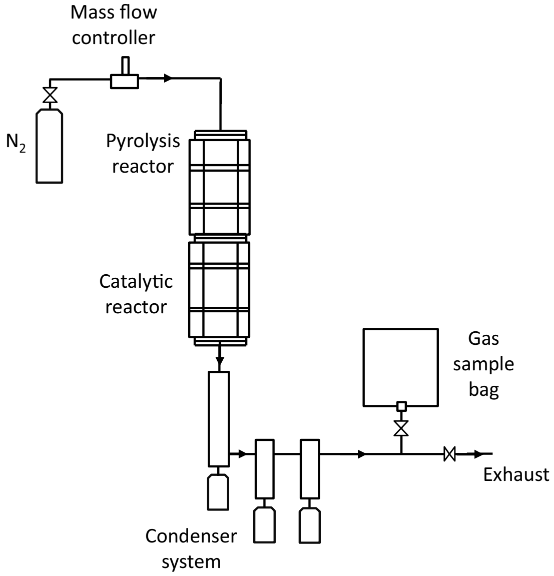

Fig. 1. Schematic diagram of the two stage pyrolysis-catalysis fixed bed reactor.

of liquid fuels. For example, thermal cracking produces evolved hydrocarbons which increase mass transfer interaction with the catalyst in the second stage, also any contaminants are retained in the first stage pyrolysis and finally the separation of the stages enables ease of recovery and recycling of the catalyst. The pyrolysis-catalysis reactor was constructed of stainless steel with dimensions of 358 mm length and an internal diameter of 20 mm. The reactor was divided into two separately heated sections consisting of the pyrolysis heated zone and catalyst heated zone heated by separately controlled and monitored electrical furnaces. The catalytic section contained a stainless steel mesh supporting quartz wool on to which the catalyst was loaded. When the mixture of the MCM-41 and ZSM-5 catalyst was used, the MCM-41 catalyst was placed before the ZSM-5 catalyst as upper and lower layers respectively (Fig. 1). The two catalysts were separated by a 5 mm layer of quartz wool. Thereby, the gases produced from the pyrolysis of the plastics in the first stage pyrolysis reactor were passed through the catalyst bed of MCM-41 and then through the catalyst bed of zeolite ZSM-5. The total mass of catalyst was always 4 g and the ratio of MCM-41 to zeolite ZSM-5 was altered to give the required ratio whilst always maintaining a catalyst mass of 4 g. A stainless steel crucible of 75 mm length and 17 mm diameter was used to hold the plastic samples in the pyrolysis section. The crucible was suspended inside the pyrolysis reactor.

Pyrolysis of the plastic (2 g) was carried out in the first stage, heating the plastic at 10 °C min^{-1} from room temperature to 500 °C. The evolved pyrolysis volatiles were passed directly to the second-stage reactor containing 4 g of catalyst which had previously been heated and was held at 500 °C. Nitrogen was used as the carrier gas to provide an inert atmosphere and to carry the product gases through the reactor. The ratio of plastic to catalyst was maintained at 1:2. Three condensers surrounded by solid dry ice were used to collect the condensable liquid products. The condenser system was connected to a Tedlar^{TM} gas sample bag for collection of non-condensable gases. After the experiment, the condensers were immediately sealed to prevent evaporation of highly volatile products and weighed to determine the total oil yield. Experiments were carried out in duplicate and showed good mass closures. Mass closure was obtained by weighing the sample crucible, catalysts and the condensers before and after experimentation. The mass of gas was calculated from the gas chromatography data and the flow of gases related to the flow rate of nitrogen purge gas and gas concentration in the gas sample bag. In fact, there was negligible mass of solid residue remaining in the sample crucible after pyrolysis and there was negligible mass of coke deposition on the catalysts.

The oil was analysed using a Varian CP3800 gas chromatography coupled to a Varian Saturn 2200 GC–MS mass spectrometer which served to identify the compounds present in the oils. The GC column was a 30m × 0.25 μm DB-5 capillary column and ion trap MS detector. Also, the oils were separately analysed using a Varian 430 GC instrument with the ZB-I column and FID (GC-FID) for the detailed quantitation of aromatic hydrocarbons. The GC–MS and GC-FID produced data for individual aliphatic and aromatic hydrocarbons enabling classification of the oils based on their gasoline range (C_8–C_{12}) and high molecular weight (C_{13+}) hydrocarbon contents. The data presented was based on peak areas calibrated in terms of response factors for standard mixtures of *n*-alkanes from C_8–C_{40} and 20 aromatic compounds.

The gas products in the gas sample bag were analysed by gas chromatography (GC) immediately at an end of each experiment. Permanent gas analysis was performed using a Varian C*P*-3380 GC with a molecular sieve column and thermal conductivity detection and hydrocarbon gases from C_1 to C_4 were analysed using a separate Varian CP-3380 GC with a HayeSep column and flame ionisation detection.

3. Results and discussion

3.1. Pyrolysis of high density polyethylene with staged catalysis

The mesoporous MCM-41 and microporous ZSM-5 zeolite catalysts were used to produce oil rich in the gasoline range hydrocarbons (C_8–C_{12}) from the pyrolysis-catalysis of high density polyethylene (HDPE). The purpose of using two catalysts staged one after the other in layers was; firstly, to induce the pre-cracking of the large molecules of pure HDPE produced from pyrolysis into smaller molecules via the larger mesopores of the MCM-41 catalyst; secondly, the resultant smaller fractions produced from the MCM-41 catalyst layer may then enter the smaller micropores of the ZSM-5 catalyst for futher cracking, mainly into a gasoline range hydrocarbon fraction [17].

3.1.1. Product yield

The catalytic cracking of pure HDPE over a staged catalyst sequence of MCM-41 followed by ZSM-5 catalysts was investigated in the two-stage pyrolysis-catalysis reactor. The ratio of feedstock plastic:catalyst used was 1:2. Different ratios of MCM-41 to ZSM-5 were investigated, being 1:1, 3:1 and 7:1. The obtained product yields are presented in Fig. 2. In addition, also presented are the results with MCM-41 and ZSM-5 zeolite alone from the pyrolysis-catalysis of high density polyethylene. A high content of gaseous

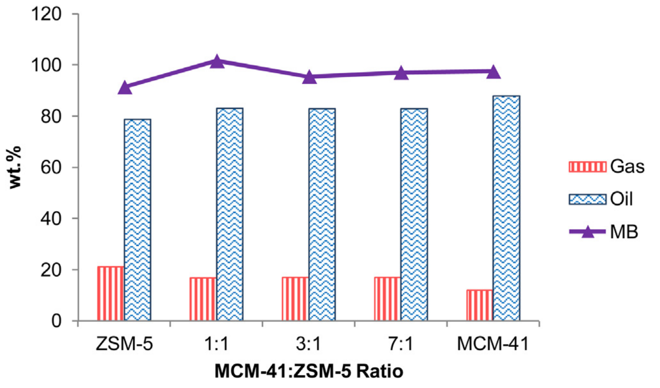

Fig. 2. Product yield and mass balance for different staged catalysts ratios (1:1, 3:1, 7:1) of MCM-41 and ZSM-5 zeolite for the catalytic pyrolysis of high density polyethylene.

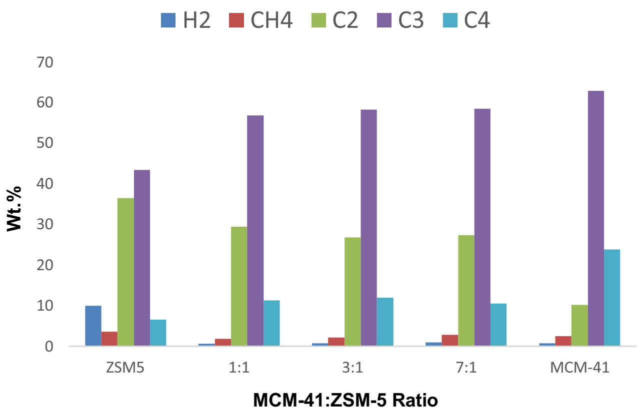

Fig. 3. Gases produced from catalytic pyrolysis of high density polyethylene with different staged catalyst ratios of MCM-41 and ZSM-5 zeolite catalysts.

product was observed when ZSM-5 zeolite catalyst was loaded alone, whereas a high content of oil product was produced over the MCM-41 catalyst. MCM-41 catalyst had Si:Al ratio much lower than that of the ZSM-5 zeolite catalyst; 4 compared to 20. Reducing Si:Al ratio serves to increase the surface acidity of the catalyst by increasing concentration of aluminium. The acidity of a catalyst provides the catalytic activity whilst the pore size provides the shape selectivity. By changing Si:Al ratio, it is possible to change the number of the acid sites. This suggests that the catalytic performance of the ZSM-5 catalyst, which has a lower number of acid sites enhances the production of gases due to the high activity for C—C bond scission, while MCM-41 acidity was appropriate to crack polyethylene into liquid hydrocarbons. The findings are consistent with those of other studies, for example, Sharratt et al. [18] reported a high content of volatile hydrocarbons, where more than 90 wt.% was achieved from catalytic pyrolysis of HDPE over HZSM-5 in a fluidized bed reactor at a temperature of 360 °C. The volatile hydrocarbons contained mainly gaseous products in the C_1–C_4 gaseous hydrocarbon range (up to 70 wt.%) with lower concentrations (~25–30 wt.%) of a gasoline hydrocarbon fraction (C_5–C_9). Manos et al. [19] reported that the liquid selectivity of ZSM-5 zeolite catalyst was only 39% and hence a high content of gases was achieved with a lower proportion of liquid.

In addition, Aguado et al. observed that the liquid product was the main product obtained from the catalytic degradation of HDPE over MCM-41 (65.2 wt.%), in contrast, the cracking of HDPE over ZSM-5 led to a high amount of gaseous hydrocarbons being produced [20].

The oil product obtained from catalytic pyrolysis of pure HDPE over different ratios of MCM-41:zeolite ZSM-5 showed only small differences in gas and oil yield in relation to the different MCM-41:ZSM-5 catalyst ratios used. A small increase in oil yield and decrease in gas yield is suggested when increasing amounts of MCM-41 catalyst were introduced to the catalyst mixture. However, as will been seen in Sections, 3.1.2. and 3.1.3., there were significant differences in composition in the product gases and oils in relation to the different MCM-41:ZSM-5 catalyst ratios used.

3.1.2. *Gas composition*

Fig. 3 shows the concentration of the product gases produced from the pyrolysis-catalysis of HDPE in relation to MCM-41 and zeolite ZSM-5 alone and also with staged catalysis using different ratios of MCM-41: zeolite ZSM-5. The data shown in Fig. 3 are the normalised wt.% of the mass of the individual gases based on the wt.% yield data shown in Fig. 2. The main gases produced were C_2 (mainly ethene), C_3 (mainly propene), and C_4 (mainly butene and butadiene) gases. The percentage of C_2 gases decreased with increasing proportions of MCM-41, while the C_3–C_4 gases increased with increasing MCM-41 content in the catalyst used. As mentioned before, the catalytic performance of ZSM-5, with a lower number of acid sites enhanced the production of gases due to the high activity for C—C bond scission, while MCM-41 acidity was appropriate to crack polyethylene into liquid hydrocarbons. Comparing the gas compositional data for the MCM-41 and zeolite ZSM-5 catalysts showed that the compositions were not exactly as expected based on the gas composition found with either MCM-41 or zeolite ZSM-5 only. This may be due to experimental error.

Sharratt et al. [18], examined the influence of a HZSM-5 catalyst with small micropore volume on the catalytic pyrolysis of HDPE. They reported a higher content of C_2 and C_3 gases, at 3.13 wt.% and 29.1 wt.%, respectively, compared with gases produced over a silica catalyst where 0.6 wt.% of C_2 and 14.0 wt.% of C_3 gases were obtained. Gobin et al. [21] suggested that catalytic pyrolysis of HDPE over ZSM-5 hindered the generation of coke. Ali et al. [22] also found that ZSM-5 led to a gaseous product distribution of C_1–C_4 gas fractions (72.6 wt.%) from the degradation of HDPE at a temperature of 360 °C in a fluidized bed reactor. The present finding also supports the work of Elordi et al. [23] who concluded that HZSM-5 catalyst contributed to the formation of light gases (C_1–C_4). They reported that 61 wt.% of C_1–C_4 gases was achieved from catalytic pyrolysis of HDPE in a conical spouted bed reactor at a temperature of 500 °C.

The contribution of MCM-41 for the production of hydrocarbon gases is consistent with the report of Aguado et al. [20]. They observed more than 50 wt.% of product were in the hydrocarbon range from C_5 to C_{12} from catalytic cracking of HDPE over MCM-41, whereas up to 40 wt.% in the range from C_2 to C_4 over ZSM-5. Seddegi et al. [24] obtained a higher content of C_4–C_8 hydrocarbon fractions from the catalytic degradation of HDPE over MCM-41, at a temperature of 450 °C in a glass batch reactor, which is in agreement with the results of the present study. Their results indicated the role of MCM-41 pore structure in the cracking mechanism, with catalysts having small pore diameters giving higher activity compared to catalysts with larger pore diameters. Compared to thermal cracking reactions, the pore structure of MCM-41 serves to stabilize the free radicals that occur during catalytic cracking, also known as free radical mechanism [24].

Fig. 3 shows a notable decrease in the amount of C_2–C_4 gases from the pyrolysis-catalysis of HDPE for the ratio of MCM-41:ZSM-5 at 7:1 corresponding to the lower proportion of ZSM-5 in the ratio, which is consistent with the literature [19]. Manos et al. [19] showed that the light gas fractions were the major product of ZSM-5. The higher ratio of ZSM-5 catalyst that was loaded, the higher amount of light gas fraction obtained.

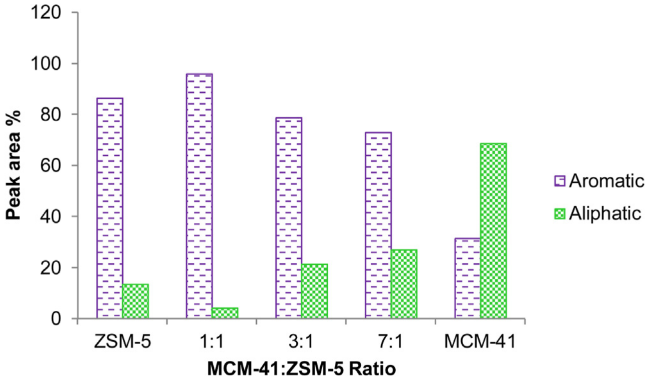

Fig. 4. Distribution of aliphatic and aromatic hydrocarbons for the catalytic pyrolysis of high density polyethylene with different stage catalyst ratios of MCM-41 and ZSM-5 zeolite catalyst.

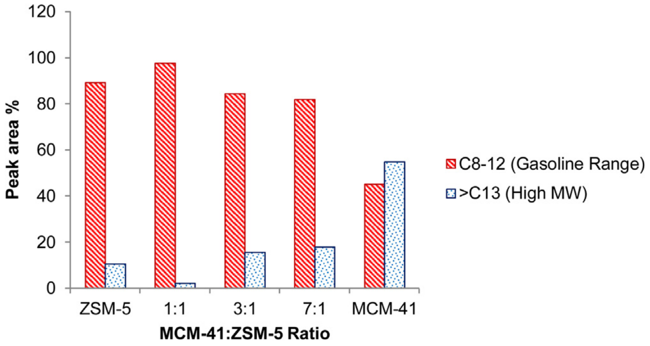

Fig. 5. Influence of different staged catalyst ratios on the distribution of gasoline range (C_8–C_{12}) and high molecular weight (C_{13+}) hydrocarbons from the catalytic pyrolysis of high density polyethylene.

3.1.3. Product oil composition

The quality of liquid product derived from the pyrolysis-catalysis of HDPE using the staged catalysts was evaluated in terms of the content of gasoline range hydrocarbons. The product yield in relation to the different MCM-41: zeolite ZSM-5 staged catalyst ratios in Fig. 2 showed that there was a slight difference in the yield of oil and gas product with the different staged catalyst ratios. However, the composition of the oils was greatly influenced by the different ratios of the staged MCM-41 and zeolite ZSM-5 catalysts and the results are shown in Fig. 4. The oil produced from catalytic pyrolysis using MCM-41 catalyst was mainly aliphatic, in contrast, using the zeolite ZSM-5 catalyst a mainly aromatic oil was produced.

Fig. 4 also shows that the aromatic contents of the product oil decreased with increasing proportions of MCM-41, followed the order of 1:1 > 3:1 > 7:1. Therefore, MCM-41 could be used in conjunction with zeolite ZSM-5 to optimise the amount of aromatic compounds produced in the final product oil in order to comply with specified aromatic contents of commercial fuels [15,16]. These results support the results of Garcia et al. [25] which concluded that a high content of aromatic compounds was achieved from catalytic pyrolysis of HDPE over a hybrid ZSM-5/MCM-41 catalyst compared to the degradation over a pure HZSM-5 catalyst.

Fig. 5 shows the influence of the ratio of MCM-41 to zeolite ZSM-5 catalysts for the pyrolysis-catalysis of HDPE using staged catalysis at different catalyst ratios in relation to the gasoline range hydrocarbons i.e. C_8–C_{12} and the higher molecular weight hydrocarbons, i.e. C_{13+}. It can be seen that the use of the ZSM-5 catalyst alone led to a high amount of gasoline range hydrocarbons, while the use of the MCM-41 catalyst alone led to high molecular weight hydrocarbons. Research findings by Sharratt et al. [18] also pointed towards the production of a gasoline range hydrocarbon fraction as the major product of HDPE catalytic pyrolysis over HZSM-5. They observed that more than 65 wt.% of a gasoline range hydrocarbon fraction was obtained from the catalytic pyrolysis of HDPE over HZSM-5 in the temperature range from 360 °C to 430 °C. Manos et al. [19] investigated the catalytic pyrolysis of HDPE over ZSM-5 and reported the production of a light hydrocarbon fraction, with less than 2% of hydrocarbons above C_{10}, due to the selectivity properties of ZSM-5. Aguado et al. [26] concluded that MCM-41 catalyst led to the formation of C_{13}–C_{40} hydrocarbon fractions. The catalytic degradation of HDPE over MCM-41 produced 12.8 wt.% of high molecular fractions in the range from C_{13} to C_{40}. Compared to MCM-41 performance, operating catalytic degradation over ZSM-5 obtained just 1.6 wt.% of high molecular weight hydrocarbons.

According to the results obtained in this study, the liquid products mainly consisted of hydrocarbons in the gasoline-range hydrocarbon fraction of C_8–C_{12} when MCM-41 and ZSM-5 were loaded as two separate layers. This findings highlight that MCM-41 catalyst with higher surface area and larger pore volume contributes to the cracking of the larger hydrocarbon compounds produced from the pyrolysis of high density polyethylene into small molecules which could then enter the pores of the ZSM-5 catalyst for reforming reactions. ZSM-5 transforms the resultant fractions from the MCM-41 catalyst layer into gasoline range hydrocarbon fractions.

The order of the highest obtained gasoline range hydrocarbon fraction in terms of the ratio of MCM-41:ZSM-5 ratio was 1:1 > 3:1 > 7:1. When a large proportion of MCM-41 catalyst was introduced to the second catalytic stage of the fixed bed reactor, the high molecular weight fraction of the product oil increased. Consequently, the gasoline range hydrocarbon fractions moderately declined.

3.2. Pyrolysis of real world waste plastics with staged pyrolysis

The results from the pyrolysis of HDPE using the staged catalysis of MCM-41 and zeolite ZSM-5 was further investigated using several 'real world' waste plastics produced from different industrial sectors. The plastic waste samples were, agricultural waste plastics (AW), building reconstruction plastics (BR), mineral water container plastics (MWC) and household food packaging waste plastics (HFP). More than half of the plastics used in the agricultural industry are low density polyethylene (65%), polyvinyl chloride (23%) and lower concentrations of other plastics. Waste mineral water bottles consists of mostly polyethylene terephthalate, but also high density polyethylene. The predominant plastic polymers in the building and construction waste stream are polyvinyl chloride, polyurethane, and polyethylene. A wide range of plastics are used in household food packaging including, polyethylene, polypropylene and polyethylene terephthalate.

In this section pyrolysis of the waste plastics was undertaken with a staged catalysis ratio of MCM-41 and zeolite ZSM-5 of 1:1 with a catalyst temperature of 500 °C.

3.2.1. Product yield

Fig. 6 presents the product yield obtained from the catalytic pyrolysis the waste plastic samples of agricultural waste (AW), mineral water containers (MWC), building reconstruction (BR), and household food packaging waste (HFP). The product yield distribution of plastic waste samples showed differences in the reactivity of specific plastic waste components. The overall mass balance for the experiments shows that excellent mass closure was achieved.

The combined staged catalytic performance of MCM-41 and ZSM-5 was effective to obtain a higher oil yield than gaseous products from the degradation of agricultural waste (AW), mineral water containers (MWC), building reconstruction (BR), and house-

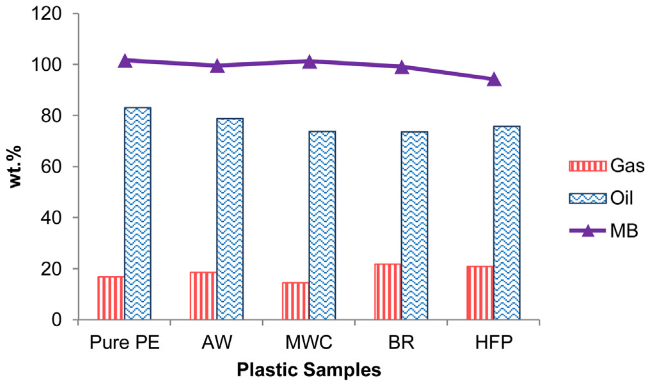

Fig. 6. Product yield and mass balance of catalytic pyrolysis of waste plastic samples: AW (Agricultural Waste), MWC (Mineral Water Containers), BR (Building Reconstruction), and HFP (Household Food Packaging Waste) (MB = Mass Balance).

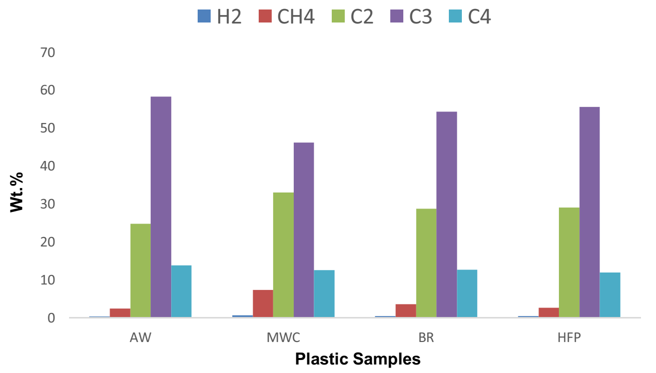

Fig. 7. Gases produced from catalytic pyrolysis of waste plastic samples: AW (Agricultural Waste), MWC (Mineral Water Containers), BR (Building Reconstruction), and HFP (Household Food Packaging Waste).

hold food packaging waste (HFP). Also, the oil yield derived from catalytic pyrolysis of waste plastic samples was lower than that from catalytic pyrolysis of pure HDPE. The order of obtained oil product yield by waste plastic samples was AW > HFP > MWC > BR. The oil and gas yields resulted from catalytic pyrolysis of waste plastic samples were comparable to that found for polyethylene, reflecting the dominance of polyethylene in the waste plastic samples. However, the waste plastic samples also produced some char, which suggests the content of PET in the waste plastic mixtures.

3.2.2. *Product gases*

Fig. 7 shows the concentration of the product gases from the catalytic pyrolysis of waste plastic samples which were agricultural waste (AW), mineral water containers (MWC), building reconstruction (BR), and household food packaging waste (HFP). The data shown in Fig. 7 are the normalised wt.% of the mass of the individual gases based on the wt.% yield data shown in Fig. 6. The main gases produced during the catalytic pyrolysis of waste plastic samples were C_2 (mainly ethene with lower concentration of ethane), C_3 (mainly propene), and C_4 (mainly butene and butadiene) gases. C_2, C_3 and C_4 gases produced from AW, BR and HFP were close to that produced from pure polyethylene. This is mostly probably due to the high content of polyethylene in these waste samples. However, MWC sample produced a higher content of char probably due to the high content of polyethylene terephthalate. Serrano et al. [27] examined the catalytic degradation of a polyalkene mixture which contained 46.5 wt.% of low density polyethylene, 25 wt.% of high density polyethylene, and 28.5 wt.% of polypropylene over HZSM-5 and MCM-41 catalysts at a temperature of 400 °C in a batch reactor. The obtained gaseous products were mostly alkene gases due to fact that polyethylene was the major constituent in the feedstock mixture. Miskolczi et al. [28] also reported a similar catalytic performance for HZSM-5 for the degradation of packaging plastics (90 wt.% of HDPE and 10 wt.% of PS) and pure HDPE. The gaseous products for both experiments were dominated by alkene gases in the range from C_2 to C_4.

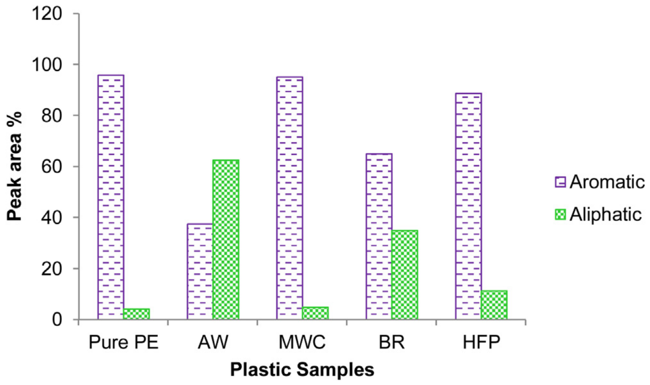

Fig. 8. Distribution of aliphatic and aromatic hydrocarbons from the catalytic pyrolysis of waste plastic samples: AW (Agricultural Waste), MWC (Mineral Water Containers), BR (Building Reconstruction), and HFP (Household Food Packaging Waste).

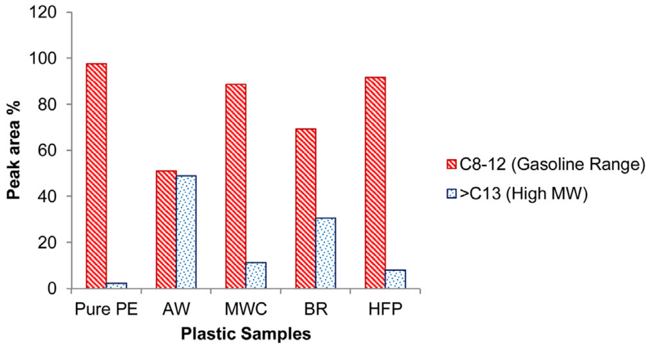

Fig. 9. Influence of different temperature of catalysts on the distribution of gasoline range (C_8–C_{12}) and high molecular weight (C_{13+}) hydrocarbons from processing of waste plastic samples: AW (Agricultural Waste), MWC (Mineral Water Containers), BR (Building Reconstruction), and HFP (Household Food Packaging Waste).

3.2.3. *Product oil composition*

The quality of liquid product was evaluated in terms of aromatics and aliphatic hydrocarbons content. Fig. 8 shows the composition of the product oils from the catalytic pyrolysis of the waste plastic samples in terms of aromatic and aliphatic content compared to the results using high density polyethylene. The mineral water containers (MWC) and household food packaging waste (HFP) produced oils with a marked aromatic content in the presence of the MCM-41 and ZSM-5 zeolite catalysts, 95.14 wt.% and 88.74 wt.%, respectively. BR also produced a high amount of aromatic compounds (64.97 wt.%). The exception was for agricultural waste which produced a high content of aliphatic compounds in the presence of the staged catalysts (MCM-41 and ZSM-5).

Fig. 9 shows the influence of the ratio of staged catalyst on the gasoline range hydrocarbons defined as C_8–C_{12} and the high molecular weight, i.e. C_{13+} hydrocarbons. By utilizing both ZSM-5 and MCM-41 catalysts in a staged, layered system, the liquid oil products were mostly distributed in the gasoline-range hydrocarbon range of C_8–C_{12}. However, a high amount of the high molecular weight hydrocarbon fraction was observed for the catalytic pyrolysis of agricultural waste. This could be due to the presence of some contaminants in the AW sample that could be deposited in the active sites of the catalysts and consequently reduce their efficiency.

Serrano et al. [27] also reported a high proportion of gasoline range hydrocarbon fraction from the catalytic cracking of a polyalkene mixture dominated by polyethylene over a HZSM-5 catalyst, whereas the selectivity toward heavy hydrocarbons (C_{13}–C_{30}) was achieved over MCM-41. Similarly, Miskolczi et al. [28] reported that a high concentration of gasoline range hydrocarbons was observed from the catalytic cracking of waste polymers which contained a high proportion of polyethylene over a HZSM-5 zeolite catalyst. Miguel et al. [29] also concluded that HZSM-5 zeolite catalyst led to the product formation of gasoline range hydrocarbons (C_8–C_{12}), whereas MCM-41 catalyst enhanced the production of heavier hydrocarbons (C_{13}).

The overall findings indicate that the two-stage catalytic pyrolysis system was effective for the production of gasoline-range hydrocarbons. Introducing MCM-41 and ZSM-5 as upper and lower catalysts in a staged system promoted a high yield and quality of the liquid product. When a ratio of MCM-41:ZSM-5 of 1:1 was used, a highly aromatic oil was produced consisting of 95.85 wt.% of the oil with more than 97 wt.% of aromatic compounds in the C_8–C_{12} range. Such a highly aromatic oil would be problematic for direct use as a gasoline fuel, since within the EU, the properties of gasoline are specified as a research octane number (RON) of more than 95 and with a maximum alkenes content of 18% v/v, aromatics of 35% v/v, and benzene 1% v/v [15]. However, the high aromatic content oil produced from the waste plastics could be used to blend with lower aromatic oil feedstocks in order to meet the characteristics of gasoline as set-out in the EU standard specifications. Combining MCM-41 in conjunction with zeolite ZSM-5 at different ratios in a staged catalyst system could be used to manipulate yield of aromatic compounds produced in the product oil, thereby matching the required aromatic content of the oil to gasoline fuel specifications.

4. Conclusions

It has been shown that using MCM-41 and ZSM-5 zeolite catalysts in a staged layered system for the two-stage catalytic pyrolysis of waste plastics is highly effective to produce a high content of gasoline range hydrocarbons in the product oil. Most favourable results were observed when MCM-41 and ZSM-5 were used at a weight ratio of 1:1 with a ratio of feedstock plastic and catalyst of 1:2. The main gases produced during the catalytic pyrolysis of the plastics were C_2 (mainly ethene), C_3 (mainly propene), and C_4 (mainly butene and butadiene) gases. The oil product for the catalytic pyrolysis of high density polyethylene contained a high yield of gasoline range hydrocarbons (C_8–C_{12}) reaching 97.72 wt.% of yield with aromatic contents of 95.85 wt.%.

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References

[1] P. Harshal, S.M. Lawankar, Waste plastic pyrolysis oil alternative fuel for CI engine – a review, Res J. Eng. Sci (2013) 26–34.
[2] PlasticsEurope, Plastics the Facts 2014/2015, Plastics Europe, Brussels, 2015.
[3] PlasticsEurope, Plastics the Facts 2014, Plastics Europe, Brussels, 2014.
[4] C. Velis (2014), Global recycling markets – plastic waste: A story for one player – China., I. International Solid Waste Association, Editor 2014, International Solid Waste Association: Vienna.
[5] C. Delgado, L. Barruetabeña, O. Salas, O. Wolf (2007) Assessment of the Environmental Advantages and Drawbacks of Existing and Emerging Polymers Recovery Processes. European Commission JRC, EUR 22939, Luxembourg.
[6] S. Kumar, A.K. Panda, R.K. Singh, A review on tertiary recycling of high density polyethylene to fuel, Resource. Conserv. Recycl. 55 (2011) 893–910.
[7] S.M. Al-Salem, P. Lettieri, J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW): A review, Waste Manage. 29 (2009) 2625–2643.
[8] S.M. Al-Salem, P. Lettieri, J. Baeyens, The valorization of plastic solid waste (PSW) by primary to quarernary routes: from re-use to energy and chemicals, Prog. Energy Combust. Sci. 36 (2010) 103–129.
[9] D.P. Serrano, J. Aguado, J.M. Escola, Developing advanced catalysts for the conversion of polyolefinic waste plastics into fuels and chemicals, ACS Catal. 2 (2012) 1924–1941.
[10] J.M. Escola, J. Aguado, D.P. Serrano, A. Garcia, A. Peral, L. Briones, R. Calvo, E. Fernandez, Catalytic hydroreforming of the polyethylene thermal cracking oil over Ni supported hierarchical zeolites and mesostructured aluminosilicates, Appl. Catal. B Environ. 106 (2011) 405–415.
[11] Y. Uemichi, M. Hattori, T. Itoh, J. Nakamura, M. Sugioka, Deactivation behaviours of Zeolite and Silica-Alumina catalysts in the degradation of polyethylene, Ind. Eng. Chem. Res. 37 (1998) 867–872.
[12] P. Gaca, M. Drzewiecka, W. Kaleta, H. Kozubek, K. Nowinska, Catalytic degradation of polyethylene over mesoporous molecular sieve MCM-41 modified with heteropoly compounds, Pol. J. Environ. 17 (2009) 25–31.
[13] Y.H. Lin, M.H. Yang, T.F. Yeh, M.D. Ger, Catalytic degradation of high density polyethylene over mesoporous and microporous catalysts in a fluidised-bed reactor, Polym. Degrad. Stabil. 86 (2004) 121–128.
[14] J. Aguado, D.P. Serrano, G. San Miguel, M. Castro, S. Madrid, Feedstock recycling of polyethylene in a two-step thermo-catalytic reaction system, J. Anal. Appl. Pyrol. 79 (2007) 415–423.
[15] V. Wagner, R. Stahl, E. Olivares, M. Morgan, E. Foukes, EU: Fuels: Diesel and Gasoline. [Online], 2015 (Available from;) http://transportpolicy.net/index.php?title=EU:_Fuels:_Diesel_and_Gasoline#Highway_Gasoline.
[16] A.G. Buekens, H. Huang, Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic waste, Resour. Conserv. Recycl. 23 (1998) 163–181.
[17] P. Hudec, FCC catalyst – key elements in refinery technology, in: 45th International Petroleum Conference, 13 June 2011, Bratislava, Slovak Republic, 2011.
[18] P.N. Sharratt, Y.H. Lin, A.A. Garforth, J. Dwyer, Investigation of the catalytic pyrolysis of high-density polyethylene over a HZSM-5 catalyst in a laboratory fluidized-bed reactor, Ind. Eng. Chem. Res. 36 (1997) 5118–5124.
[19] G. Manos, A.A. Garforth, J. Dwyer, Catalytic degradation of high-density polyethylene over different zeolitic structures, Ind. Eng. Chem. Res. 39 (2000) 1198–1202.
[20] J. Aguado, J.L. Sotelo, D.P. Serrano, J.A. Calles, J.M. Escola, Catalytic conversion of polyolefins into liquid fuels over MCM-41: Comparison with ZSM-5 and mmorphous SiO_2-Al_2O_3, Energy Fuel 11 (1997) 1225–1231.
[21] K. Gobin, G. Manos, Polymer degradation to fuels over microporous catalysts as a novel tertiary plastic recycling method, Polym. Degrad. Stabil. 83 (2004) 267–279.
[22] S. Ali, A.A. Garforth, D.H. Harris, D.J. Rawlence, Y. Uemichi, Polymer waste recycling over used catalysts, Catal. Today 75 (2002) 247–255.
[23] G. Elordi, M. Olazar, G. Lopez, M. Amutio, M. Artetxe, R. Aguado, J. Bilbao, Catalytic pyrolysis of HDPE in continuous mode over zeolite catalysts in a conical spouted bed reactor, J. Anal. Appl. Pyrolysis 85 (2009) 345–351.
[24] Z.S. Seddegi, U. Budrthumal, A.A. Al-Arfaj, A.M. Al-Amer, S.A.I. Barri, Catalytic cracking of polyethylene over Al-Silica MCM-41 molecular sieve, Appl. Catal. A Gen. 225 (2002) 167–176.
[25] R.A. García, D.P. Serrano, D. Otero, Catalytic cracking of HDPE over hybrid zeolitic–mesoporous materials, J. Anal. Appl. Pyrolysis 74 (2005) 379–386.
[26] J. Aguado, D.P. Serrano, J.L. Sotelo, R.V. Grieken, J.M. Escola, Influence of the operating variables on the catalytic conversion of a polyolefin mixture over HMCM-41 and nanosized HZSM-5, Ind. Eng. Chem. Res. 40 (2001) 5696–5704.
[27] D.P. Serrano, J. Aguado, J.M. Escola, Catalytic cracking of a polyolefin mixture over different acid solid catalysts, Ind. Eng. Chem. Res. 39 (2000) 1177–1184.
[28] N. Miskolczi, L. Bartha, G. Deák, Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts into fuel-like feed stocks, Polym. Degrad. Stabil. 91 (2006) 517–526.
[29] G.S. Miguel, D.P. Serrano, J. Aguado, Valorization of waste agricultural polyethylene film by sequential pyrolysis and catalytic reforming, Ind. Eng. Chem. Res. 48 (2009) 8697–8703.