

Thermo-catalytic pyrolysis of waste polyethylene bottles in a packed bed reactor with different bed materials and catalysts

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ABSTRACT

Plastic waste is an increasing economic and environmental problem as such there is a great need to process this waste and reduce its environmental impact. In this work, the pyrolysis of high density polyethylene (HDPE) waste products was investigated using both thermal and catalytic cracking techniques. The experimental work was carried out using packed bed reactor operating under an inert atmosphere at 450 °C. Different reactor bed materials, including sand, cement and white clay were used to enhance the thermal cracking of HDPE. In addition, the catalytic effect of sodium hydroxide, HUSY and HBeta zeolite catalysts on the degradation of HDPE waste was also investigated. The reactor beds were found to significantly alter the yield as well as the product composition. Products such as paraffins ($\leq C_{44}$), olefins ($\leq C_{22}$), aromatics ($\leq C_{14}$) and alcohols (C_{16} and C_{17}) were obtained at varying rates. The highest yield of liquid (82%) was obtained over a cement powder bed with a paraffin yield of 58%. The yield of paraffins and olefins followed separate paths, for paraffins it was found to increase in the order of Cement > White clay > Silica Sand, whereas for the olefins it was in the reverse order Silica Sand > White clay > Cement. The results obtained in this work exhibited a higher P/O ratio than expected, where the amount of generated paraffins was greater than 60% in most cases. Less olefin was generated as a consequence. This indicates that the product generated is more suited to be used as a fuel rather than as a chemical feedstock. The carbon chain length was narrowed to C_{10} – C_{28} when the zeolitic catalysts were employed, as well as a significant yield of aromatics was obtained mainly naphthalene and α -limonene as an indication that the products obtained are fuel-like products.

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1. Introduction

Plastics are affordable, durable, versatile and favorably used in manufacturing due to their light weight, strength and chemical resistance; thus they can be easily tailored to meet various consumer and market needs. High density polyethylene (HDPE) polymer is the third largest commodity plastic material in the world, after polyvinyl chloride and polypropylene in terms of volume. However, plastics are non-biodegradable and impose an ever growing environmental burden [1]. Plastic waste management in Europe is distributed between 53% land filling, 29% incineration, 16% mechanical recycling and 2% feedstock recycling [2]. The conventionally used methods to handle plastic waste, such as land filling, are no longer sustainable as they can cause toxic fires, air pollution, ground water contamination and irreversible soil

damage. Also incineration has its own share of the blame in causing controversial health and environmental damages. Mechanical recycling recovers plastic waste into a product of lower quality and strength. In addition, the quality of the recycled product deteriorates further with every recycling cycle. Feedstock recycling on the other hand is the direct conversion of plastic waste into valuable and useful chemicals such as fuel or as raw materials (monomers) for the polymer industry. Thermal pyrolysis is considered one of the most attractive feasible techniques which involve the degradation of the polymeric materials by heating in the absence of oxygen [3]. Pyrolysis is useful to break down the waste plastics into three products; wax, liquid and gas in an inert environment. The liquid is attractive because its properties show its potential for use as chemical feedstock or fuel.

The thermal and catalytic degradation of polyethylene has been the subject of numerous studies by researchers who investigated the effect of temperature, residence time, reactor design and catalyst on the degradation process, and more precisely on the

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distribution of the products generated and their composition [4–10]. William et al. [11] studied the effect of reaction temperature ranging from 500 to 700 °C on the composition of the products obtained from LDPE pyrolysis. The increase in temperature led to a significant increase in single and polycyclic aromatics in the derived oil that necessitated further treatment. The produced wax contained aliphatics and no aromatics with potential utilization in the petrochemical feedstock. Artetxe et al. [12] proposed a two-step (thermal and catalytic) reaction system for HDPE valorization followed by a catalytic packed bed reactor with a catalyst based on a HZSM-5. An increase in temperature or space–time increased the yield of light olefins and decreases the yield of C₁₂⁺ hydrocarbons or non-aromatic C₅–C₁₁ fraction. Furthermore, an increase in space–time and temperature enhances secondary reactions and, therefore, the yield of the single-ring aromatic fraction. The yield of waxes was negligible even at low temperatures or spaces-times. Liu et al. [13] investigated the catalytic reforming of the pyrolytic intermediates from the co-pyrolysis of pubescens and LDPE over the parent and desilicated zeolite ZSM-5 (DeZSM-5). The parent HZSM-5 exhibited high aromatization activity, whereas DeZSM-5 exhibited high alkanisation activity in the pyrolysis of LDPE. The aromatization was favored mainly by strong acid sites and the alkanisation was facilitated chiefly by weak acid sites in catalyst ZSM-5. The total relative content of phenolic compounds in aqua obtained by vapor-catalyzed co-pyrolysis was very high (60–65%) compared to thermal co-pyrolysis (26.94%). The thermal and catalytic pyrolysis of LDPE and HDPE over HZSM5 and HUSY have been studied under dynamic conditions in a batch reactor [14]. The amount of gases generated drastically increases when catalysts were employed, especially with HZSM5, whilst liquids and the coke deposit were more abundant with HUSY. For the HZSM5 zeolite, olefins were the major compounds in the gas fraction, followed by 1-olefins, n-paraffins and iso-paraffins, whilst in the liquid fraction; aromatics were by far the major compounds. Similarly, for gases generated in the presence of HUSY, olefins were the major compounds, whilst also appreciable quantities of iso-paraffins, 1-olefins and n-paraffins were obtained. With the HZSM5 zeolite, the high yields achieved for propene, 2-methyl-2-butene and isobutene were remarkable. For HUSY, the major compounds were 2-cis-butene, propene, isoprene and isobutane, formed in substantially lower yields than with HZSM5. Shah et al. [15] investigated a wide range of acidic and basic catalysts like silica, calcium carbide, alumina, magnesium oxide, zinc oxide and homogeneous mixture of silica and alumina for the conversion of waste polyethylene. CaC₂ was better on the basis of reaction time, however the efficiency of conversion into liquid for SiO₂ was found to be maximum in case of LDPE at optimum conditions. The results of the column separation using different solvents indicate that the oxide containing catalyst could be best suited for selective conversion

into polar and aromatic products while CaC₂ could be adopted for selective conversion into aliphatic products.

In this work, the pyrolysis of high density polyethylene (HDPE) waste products was investigated using both thermal and catalytic cracking techniques. The experimental work was carried out using packed bed reactor operating under an inert atmosphere at 450 °C. Different reactor beds, including sand, cement and white clay were used to enhance the thermal cracking of HDPE. In addition, the catalytic effect of sodium hydroxide, HUSY and HBeta zeolite catalysts on the degradation of HDPE waste was also investigated.

2. Materials and methods

2.1. Materials

Waste high density polyethylene (HDPE) was obtained from collected used shampoo bottles. These were flushed and cleaned with distilled water, cut and grinded into small portions of 3–5 mm diameter. Silica sand (SiO₂) with particle size of 250 µm and bed depth of 4 cm was used as a reactor bed material. The same bed depth was used for cement powder and white clay. The composition of sand, clay and cement powder were all determined using X-ray Diffraction (XRD). Sand was found to be mainly composed of Silica Oxide (SiO₂), cement was composed of a mixture of several compounds; of which are Hatrurite, (Ca₃SiO₅) and Chromium (Cr); whereas white clay was composed of Bassanite (CaSO₄·0.5H₂O). Sodium hydroxide pellets (NaOH), obtained from Sigma Aldrich, were used as basic catalyst; while HUSY (surface area: 660 m²/g, SiO₂/Al₂O₃ = 5.2 M ratio) and HBeta (surface area: 620 m²/g, SiO₂/Al₂O₃ = 300 M ratio), obtained from Zeolyst International, were used as acidic catalyst.

2.2. Packed bed reactor

The laboratory setup for conducting pyrolysis experiments involved a packed bed reactor built in-house (Fig. 1). The reactor rig is 16 cm height × 8 cm diameter stainless steel equipped with a high-temperature resistant gasket (1000 °C), nitrogen inlet port, 5 bar relief valves and a gas outlet port. Tubes are stainless steel quarter inch OD, and the condensate tank is 2 L. The reactor bed was kept constant at 14 cm in all experiments. The pyrolysis experiments were conducted at 450 °C, 1 bar and maintained at the desired temperature for 45 min. The temperature was monitored with a K-type thermocouple placed in the center of the reactor. The reactor contents were purged continuously with high-purity nitrogen (N₂) at a flow of 0.2 L/min to ensure oxygen free medium.

Two types of experiments were carried out: (1) effect of different reactor bed material (sand, cement powder and white clay); (2) effect of catalyst type (NaOH, HUSY and HBeta). In each

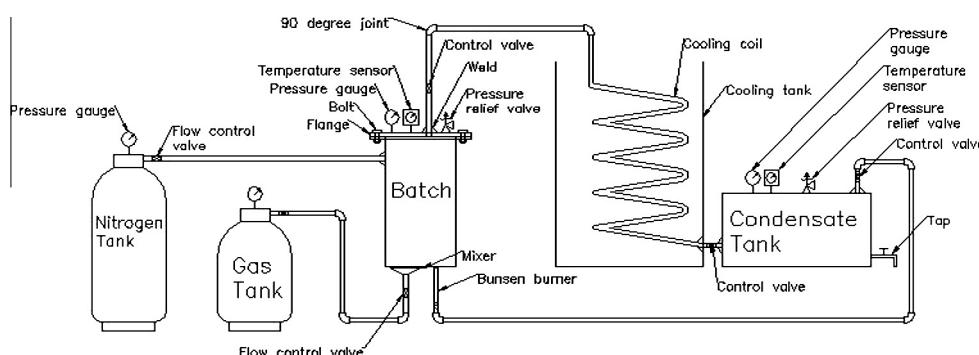


Fig. 1. Experimental setup.

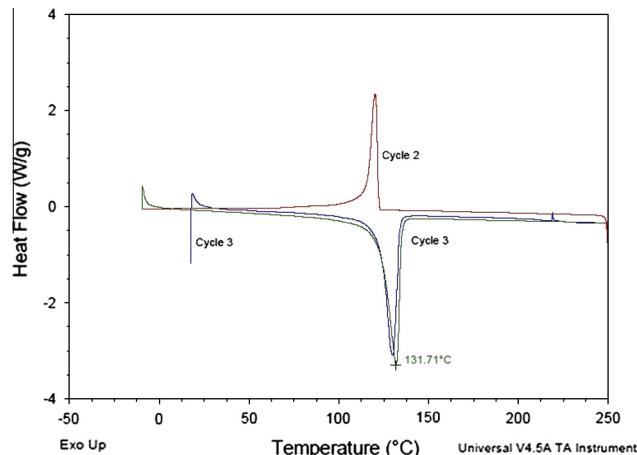


Fig. 2. DSC of high density polyethylene (HDPE).

experiment, 10 g of grinded waste HDPE were placed in the reactor; the material bed was added, and the reactor was then closed and pressurized with air to ensure no leakages. The reactor was then pre-purged with nitrogen for 10 min and then heated. The waste HDPE was first converted to their molten state at temperatures ranging between 130 and 135 °C. This was predetermined using Differential Scanning Calorimeter (DSC Q 2000) which showed one peak at 131.7 °C (Fig. 2). HDPE was cracked afterwards at a temperature range of 400–450 °C (Fig. 3). The evolved gases from the pyrolysis reaction were then passed through a cooling coil to the condenser and then to the condensate tank to be collected as liquid/wax and gas. At the end of each experiment, liquid and wax products were collected, weighed and dissolved in dichloromethane (DCM) GC grade. These compounds were identified and quantified by a Thermo GC-MS provided with HP-5MS column with heating rate of 12 °C/min.

3. Results and discussion

3.1. Thermal degradation

The product yields from the thermal degradation of waste HDPE at 450 °C are shown in Fig. 4. The wax obtained was lightly viscous and had a yellow color, whereas the light green liquid was mixed with dark brown heavy oil. It is worth mentioning that when the same experiment was carried out without any bed material in the reactor, the product yield gave 100% wax of high viscosity and dark yellow color. The silica sand bed produced the largest amount of gases at 51%, while the liquid yield reached 40% and that of wax was 9%. The cement powder bed produced the largest amount of liquids at 82% with a gas yield of 18%. These results were compared with other results reported by different researchers.

The GC-MS analysis (Fig. 5, Table 2) showed that all reactor beds produced paraffins with carbon chain number ranging from C_{10} to C_{44} . When a silica sand bed was used, the olefines were distributed between C_{10} and C_{22} . On the other hand, the cement bed produced the narrowest olefines distribution over a range from C_{10} to C_{15} . The white clay bed gave a slightly broader distribution over a C_{10} – C_{19} range. Heneicosane ($C_{21}H_{44}$) was the dominant component among all paraffins, while tridecene ($C_{13}H_{26}$) and nonadecene ($C_{19}H_{38}$) were dominant in the olefins. α -limonene ($C_{10}H_{16}$) was present in almost all samples as the most abundant aromatic compound. Alcohols such as hexadecanol ($C_{16}H_{34}O$) and heptadecanol ($C_{17}H_{36}O$) were obtained with all beds except with silica sand.

Aromatics containing, α -limonene ($C_{10}H_{16}$) and cyclotetradecane ($C_{14}H_{28}$) were produced at the highest combined yield of 9.2% when a silica sand bed was utilized. Cyclotetradecane ($C_{14}H_{28}$) disappeared in other reactor beds, and the overall aromatics contents were decreasing in the order of Silica Sand > Cement > White clay. The cement powder bed produced the highest yield of α -limonene ($C_{10}H_{16}$) with 6.3%. The presence of aromatics in thermal pyrolysis is one of the main characteristics of HDPE. The yield of paraffins and olefins followed separate paths, for

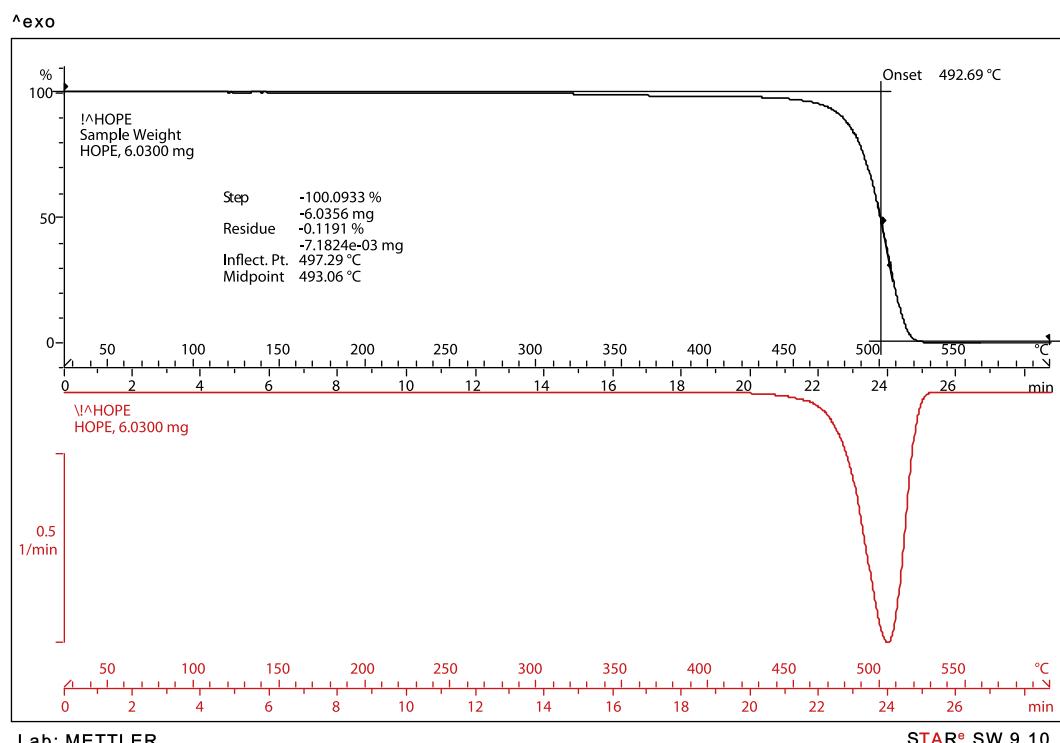


Fig. 3. TGA of high density polyethylene (HDPE).

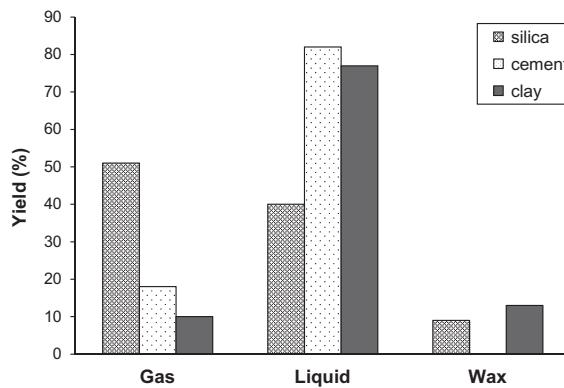


Fig. 4. Product yield from the pyrolysis of waste HDPE at 450 °C using different reactor bed materials.

paraffins it was found to increase in the order of Cement > White clay > Silica Sand. Whereas for the olefins it was in the reverse order Silica Sand > White clay > Cement. Furthermore, the paraffin to olefin ratio, P/O, was about 1 when silica sand was used. However, it was the double when cement powder was used. Sand contains more silica than clay and cement, and it is this high silica contents that determines the acidity of the employed bed. A high acidity will result in a lower P/O ratio as is the case here. Hence, it is obvious that varying the reactor bed material is greatly influencing the product selectivity and yield due to the various acidities of the used beds.

3.2. Catalytic degradation

In the catalytic reactions, each catalyst (NaOH, HUSY and HBeta) was tested with different reactor beds. The vapor contact method was used where the catalyst layer was on top of the reactor bed layer. The product yield from the catalytic degradation of HDPE waste were carried out at 450 °C and shown in Figs. 6 and 7. The silica sand bed with NaOH produced the largest amount of liquid at 81%, while the gas yield reached 19% and no wax was obtained. Both catalysts, HUSY and HBeta, gave the highest yield of gases with silica sand, 73% and 81% yields respectively.

The yield of products obtained when employing either HUSY or HBeta as a catalyst was changed significantly when the reactor bed material changed. HBeta gave the highest yield of liquid at 67% when the reactor was packed with cement; however the case was different when employing HBeta catalyst with silica sand and white clay. The yields were 81% for gas, 15% for liquid and

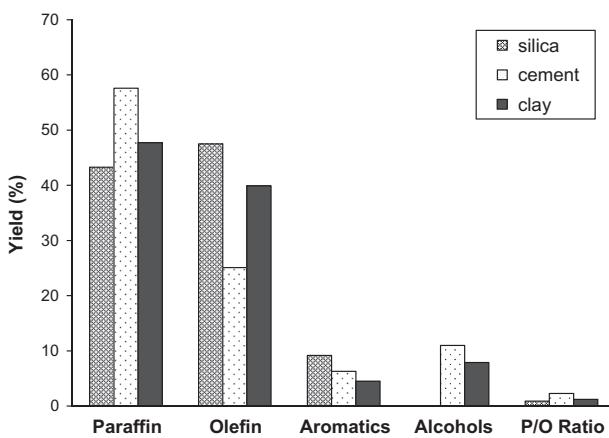


Fig. 5. Species yield from pyrolysis of waste HDPE at 450 °C using different reactor bed materials. P/O: paraffin to olefin ratio.

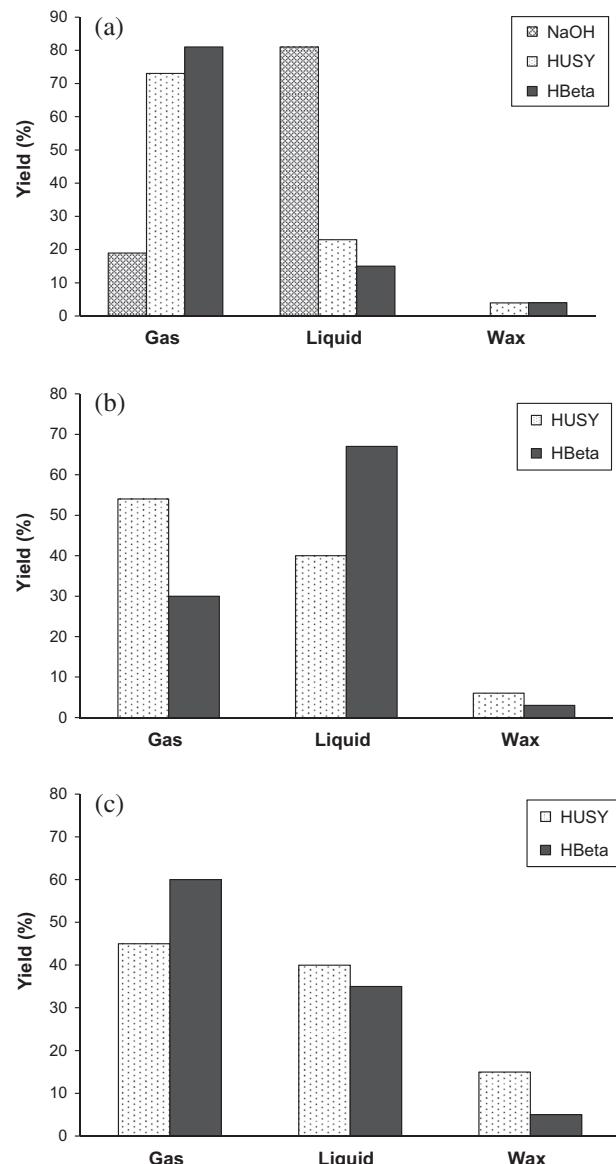


Fig. 6. Product yield from the catalytic degradation of waste HDPE at 450 °C (a) Silica Sand; (b) Cement; (c) Clay.

4% for wax when silica was used. However, when white clay was used the yield changed to 60% for gas, 35% for liquid and 5% for wax. The catalyst HUSY gave slightly higher yield of gas (54%, 45%) than liquid (40%, 40%) when employed with cement and white clay beds, respectively. The yield of wax (15%) was the highest when white clay was used. The GC-MS analysis (Table 1) showed that under a silica sand–NaOH reactor bed the carbon chain number of the obtained olefins was in the range of C₁₀–C₄₄. When silica sand was used with either HUSY or HBeta, the carbon chain number of paraffins was narrowed to C₁₀–C₂₈. A similar result was obtained with cement powder and white clay beds; the carbon chain number in the paraffins ranged from C₁₀ to C₂₉ and from C₁₀ to C₃₅ with HUSY, and from C₁₁ to C₂₉ and C₁₀–C₃₆ with HBeta. The olefins were distributed between C₁₀ and C₂₃ with beds/catalysts of silica sand–NaOH, cement–HBeta, white clay–HUSY and white clay–HBeta. On the other hand, the obtained olefins in the cement–HUSY and silica sand–HBeta beds were the narrowest. They ranged from C₁₁ to C₁₈ and from C₁₅ to C₁₉, respectively. However, no olefins were obtained with the silica sand–HUSY bed reactor. Octacosane (C₂₈H₅₈) was the dominant

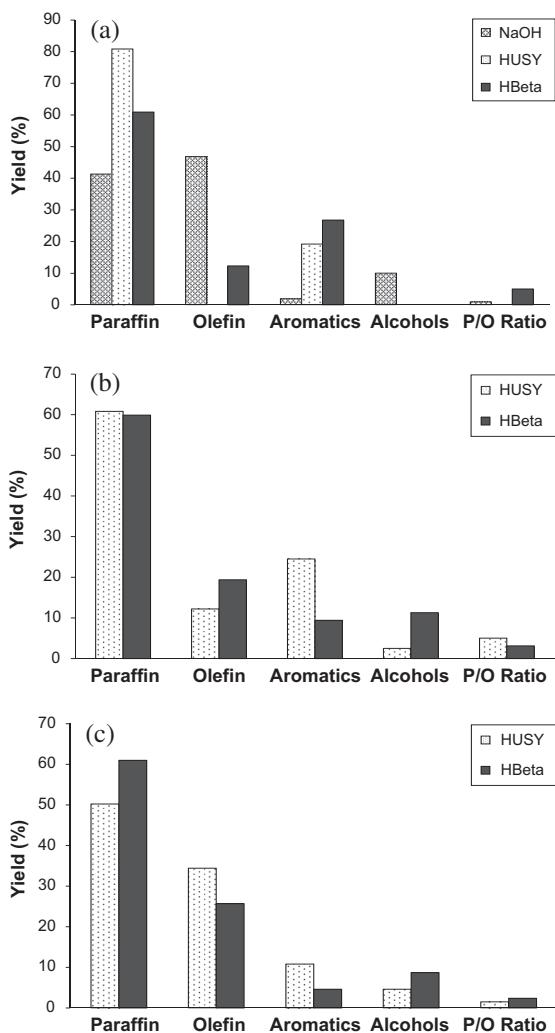


Fig. 7. Species yield from the catalytic degradation of waste HDPE at 450 °C (a) Silica Sand; (b) Cement; (c) Clay.

component among all paraffins under silica sand-HUSY bed (17.7%), white clay-HBeta (11%), cement-HUSY (8.5%) and silica sand-NaOH (7%). Nonadecane ($C_{19}H_{40}$), heneicosane ($C_{21}H_{44}$) and heptadecane ($C_{17}H_{36}$) were the dominant component in the paraffins obtained with beds containing silica sand-HBeta, cement-HBeta and white clay-HUSY. Nonadecene ($C_{19}H_{38}$) was the dominant product in the olefins for all bed reactors except for silica sand-HBeta and cement-HUSY where hexadecene ($C_{16}H_{32}$) and dodecene ($C_{12}H_{24}$) were the dominant olefins obtained. D-limonene ($C_{10}H_{16}$) was present in almost all samples as the most abundant aromatic compound; however cyclotetradecane ($C_{14}H_{28}$) was the dominant aromatic compound for cement-HBeta and white clay-Hbeta bed reactors. 1,7-Dimethyl Naphthalene ($C_{12}H_{12}$) was the dominant aromatic obtained with the reactor bed silica sand-HBeta. Alcohols such as hexadecanol ($C_{16}H_{34}O$) and heptadecanol ($C_{17}H_{36}O$) were obtained with silica-NaOH, cement-HUSY and cement-HBeta. Heptacosanol ($C_{27}H_{42}O$) and eicosanol ($C_{20}H_{42}O$) were obtained in the white clay-HUSY and white clay-HBeta bed reactors respectively. Note that no alcohol compounds were detected neither with silica sand-HUSY nor silica sand-HBeta bed reactors.

The results obtained in this work exhibited a higher P/O ratio than expected, where the amount of generated paraffins was

Table 1
GC-MS liquid product composition from the pyrolysis of waste HDPE using silica sand bed at 450 °C.

	Formula	%
<i>Alkane</i>		
Decane	$C_{10}H_{22}$	1.6
Undecane	$C_{11}H_{24}$	2.3
Dodecane	$C_{12}H_{26}$	2.6
Tridecane	$C_{13}H_{28}$	3.2
Tetradecane	$C_{14}H_{30}$	3.4
Pentadecane	$C_{15}H_{32}$	2.7
Hexadecane	$C_{16}H_{34}$	3.1
Heptadecane	$C_{17}H_{36}$	2.8
Nonadecane	$C_{19}H_{40}$	6.1
Heneicosane	$C_{21}H_{44}$	13.2
Octacosane	$C_{28}H_{58}$	1.5
Tetratetracontane	$C_{44}H_{90}$	0.8
Total		43.3
<i>Alkene</i>		
1-Decene	$C_{10}H_{20}$	4.7
5-Undecene	$C_{11}H_{22}$	0.4
1-Dodecene	$C_{12}H_{24}$	5.9
1-Tridecene	$C_{13}H_{26}$	19.8
1-Hexadecene	$C_{16}H_{32}$	3.2
1-Nonadecene	$C_{19}H_{38}$	10.2
1-Docosene	$C_{22}H_{44}$	3.2
Total		47.4
<i>Aromatics</i>		
d-limonene	$C_{10}H_{20}$	1.6
Cyclotetradecane	$C_{14}H_{28}$	7.4
Total		9

Table 2
GC-MS liquid product composition from the pyrolysis of waste HDPE waste in a silica sand bed with NaOH catalyst at 450 °C.

	Formula	%
<i>Alkane</i>		
Decane	$C_{10}H_{22}$	1.3
Undecane	$C_{11}H_{24}$	2.0
Dodecane	$C_{12}H_{26}$	2.3
Tridecane	$C_{13}H_{28}$	2.6
Tetradecane	$C_{14}H_{30}$	2.5
Pentadecane	$C_{15}H_{32}$	3.9
Octadecane	$C_{18}H_{38}$	2.8
Nonadecane	$C_{19}H_{40}$	3.4
Eicosane	$C_{20}H_{42}$	3.1
Heneicosane	$C_{21}H_{44}$	5.9
Octacosane	$C_{28}H_{58}$	7.0
Tetratetracontane	$C_{44}H_{90}$	4.5
Total		41.3
<i>Alkene</i>		
1-Decene	$C_{10}H_{20}$	4.7
1-Dodecene	$C_{12}H_{24}$	0.4
1-Tridecene	$C_{13}H_{26}$	12.2
1-Pentadecene	$C_{15}H_{30}$	5.6
1-Hexadecene	$C_{16}H_{32}$	6.4
1-Nonadecene	$C_{19}H_{38}$	12.2
1-Docosene	$C_{22}H_{44}$	5.3
Total		46.8
<i>Aromatics</i>		
d-limonene	$C_{10}H_{20}$	1.9
Alcohol		
1-Hexadecanol	$C_{16}H_{34}O$	6.2
1-Heptadecanol	$C_{17}H_{36}O$	3.8
Total		10.0

greater than 60% in most cases. Less olefin was generated as a consequence. This indicates that the product generated is more suited to be used as a fuel rather than as a chemical feedstock. These major differences achieved with the use of zeolite catalysts,

especially in terms of the obtained lighter products, are due to the micro-mesoporous nature of the catalytic structure along with high catalyst acidities. The network of pores increases the selectivity towards lighter products, and boosts the octane (aromatics) yield by reducing the effects of bimolecular reactions involving hydrogen transfer. In this work the carbon chain ranged between C₁₀ and C₂₈ with the use of acidic catalysts compared to a range of C₁₀–C₄₄ when thermal degradation was employed. In addition, certain aromatic products such as limonene and naphthalene were produced significantly in the catalytic experiments (>10%) while these aromatic compounds decreased to less than 10% during the thermal degradation experiments.

4. Conclusions

In this work, the effect of different reactor bed materials (silica sand, cement and white clay) as well as catalyst type (sodium hydroxide, HUSY and HBeta zeolite) on the degradation of high density polyethylene (HDPE) waste bottles in a packed bed reactor was investigated. The bed materials altered the lumped product yield as well as the composition of the products. C₁₀–C₄₄ paraffins and C₁₀–C₂₂ olefins were obtained along with aromatics and alcohols at varying compositions. The use of acidic catalysts narrowed the carbon chain length of the paraffins to C₁₀–C₂₈, and altered the composition of the products. Selecting an appropriate bed material with a specific catalyst refined the generated pyrolysis liquids to become similar to fuel compounds. It was concluded that a cement powder bed material was the most appropriate for the production of high liquid yield and low aromatic compounds content, as for the catalytic degradation the combination of cement bed with HBeta catalyst gave the highest yield of liquid with the smallest paraffins and carbon chain length of C₁₁–C₂₉. The employed reactor bed materials have demonstrated their effectiveness in generating fuel-like products even without using expensive catalysts.

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