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Research Article

Catalytic pyrolysis of waste high-density (HDPE) and low-density polyethylene (LDPE) to produce liquid hydrocarbon using silica-alumina catalyst

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ABSTRACT

Catalytic pyrolysis of waste HDPE and LDPE polyethylene was successfully carried out using a silica-alumina catalyst at 450 °C under N_2 atmosphere. The synthesized silica-alumina is mesoporous and shows type IV isotherm. Thermal pyrolysis (without any catalyst) provided 47% wax-like hydrocarbons at 485 °C. On the other hand, more than 80% liquid yield was achieved using silica-alumina catalysts from waste HDPE and LDPE. The highest liquid yield was obtained from LDPE (87.69%) than HDPE (83.25%) at a catalyst-to-plastic ratio of 1:25. The ^{1}H NMR shows that the liquid product does not contain any aromatic compound. The GC-MS, ^{1}H NMR, and FTIR confirmed that the liquid contains linear and branched alkanes and alkenes.

Introduction

Plastics are extensively used in our day-to-day life. For this reason, a significant amount of plastic waste is generated globally (Rahman et al., 2022). In 2018, 360 million metric tons of plastics were produced (Yang et al., 2022; Fu et al., 2023). About 6300 million metric tons of plastic waste have been generated globally from 1950 to 2015 (Geyer et al., 2017; Fu et al., 2023). Only 9% of these plastic wastes are recycled, 12% are incinerated, and the remaining 79% are disposed of in landfills (Geyer et al., 2017; Fu et al., 2023). As a developed country, the USA generated around 35.4 million tons of plastics in 2017 (Rahman et al., 2022). The USA recycled only 8.4% of plastics, incinerated 16%, and the remaining 40% was landfilled (Rahman et al., 2022). Thus, plastic waste is causing significant environmental pollution.

Plastic wastes can be converted to liquid fuel using suitable catalysts. Catalytic pyrolysis occurs at low temperatures and takes a shorter time than thermal pyrolysis (without using any catalysts). Over the years, numerous catalysts have been developed for obtaining better gasoline selectivity and converting waste plastics to liquid fuel. Catalysts developed so far for the degradation of polyolefins are mostly based on zeolite HZSM-5 (Aguado et al., 1997;Lin et al., 2004; López et al., 2011; Sivagami et al., 2022), Zeolite-Y(Manos et al., 2001; Shoaib et al., 2021), silica-alumina (SiO_2-Al_2O_3) (Aguado et al., 1997; Uddin et al., 1997), mesoporousaluminosilicate (MCM-41) (Aguado et al., 1997; Lin et al., 2004), FCC catalysts and clays (Manos et al., 2001; Rahman et al., 2022).

The catalytic activity of polyolefin degradation increases with increasing number of acid sites. However, a highly acid catalyst will provide more gaseous products than liquid. For example, HZSM-5 zeolite, which is highly acidic, mostly gives gaseous hydrocarbon (C_2-C_4, 50% of the product) (Aguado et al., 1997). On the other hand, catalysts with medium acid sites (SiO_2-Al_2O_3, MCM-41) result in gasoline

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(C_5-C_{12}) and middle distillates (C_{13}-C_{22}) (Aguadoet al., 1997). Aguado et al. (1997) pyrolyzed model virgin HDPE and LDPE pellets obtained from REPSOL by ZSM-5, MCM-41, and SiO_2-Al_2O_3 catalysts. They found that ZSM-5 catalysts provided a significant amount of gaseous hydrocarbons (C_2-C_4) (50% is gaseous product), whereas MCM-41 and amorphous SiO_2-Al_2O_3 catalysts provided mostly liquid products with boiling points in the range of gasoline (C_5-C_{12}) and middle distillates (C_{13}-C_{22}).

Zeolites are microporousaluminosilicates and are used as catalysts and adsorbents. Serrano et al.(2002)used nano-crystalline ZSM-5 zeolite for pyrolysis of HDPE and LDPE and found that 100% of the gaseous hydrocarbons (C1-C5) are produced at a temperature of 340 °C. The nano-crystalline ZSM-5 zeolite is found to be more active than ZSM-5 in producing gaseous products.

Lin et al. (2004). pyrolyzed HDPE (MW 75, 000) using MCM-41, ZSM-5, and a mixture of MCM-41/ZSM-5. They found that the HZSM-5 catalyst produced higher amounts of gaseous hydrocarbon than MCM-41 and a mixture of MCM-41/ZSM-5. For example, pyrolysis of HDPE by MCM-41catalyst provided 87.88% gaseous hydrocarbon and 3.04% liquid product. The ZSM-5 catalyst provided 94.21% gaseous products and only 1.26% liquid. The combination of ZSM-5/MCM-41 catalyst provided less gaseous product (91.45% gaseous product and 3.58% liquid) than only using ZSM-5 (Lin et al., 2004).

Shoaib et al. (2021) pyrolyzed HDPE and LDPE using zeolite Y and found that pyrolysis of both HDPE and LDPE provided 71% liquid at 450 °C at a catalyst-to-plastic ratio of 1:5.

Manos et al. (2001) used clay and ultrastable Y zeolite to crack HDPE and found that clay catalysts can provide higher amounts of liquid than Y zeolite. The clay catalyst provided 68% liquid, whereas ultrastable Y zeolite provided 44% (Manos et al., 2001). The milder acidity of clays is believed to provide a higher amount of liquid. The strong acidity of ultrastable Y zeolite promotes cracking, leading to the formation of more gaseous products.

Achilias et al. (2007) investigated the pyrolysis of polyethylene (LDPE and HDPE) and polypropylene (PP) in a laboratory fixed-bed reactor with an FCC catalyst. They found that pyrolysis of the plastic bag made from LDPE leads to mainly gasoline region C_7–C_{12} hydrocarbons. A series of hydrocarbons (alkanes and alkenes) are present in the liquid product.

Traditionally, zeolite catalysts provide less liquid products and more gaseous hydrocarbons in plastic pyrolysis due to the acidity of the catalysts. However, mesoporous silica-alumina catalysts have a higher acidity than zeolite catalysts. This study aims to understand the effect of less acidic mesoporous silica-alumina (SiO_2-Al_2O_3) catalysts on real-life single-used waste HDPE and LDPE plastic pyrolysis.

Experimental

Materials and Methods

Tetraethyl orthosilicate, aluminum isopropoxide, HCl, isopropyl alcohol, and aqueous ammonia were purchased from Sigma Aldrich, Germany. Waste HDPE (bottles) and LDPE (polyethylene bags) were collected from Dhaka city. The melting points of HDPE and LDPE are 126 °C and 110 °C, respectively. The carbon and hydrogen content of HDPE are 66.10 wt% and 26.93 wt%. The carbon and hydrogen content of LDPE are 77.72 wt% and 21.67 wt%.

Synthesis of silica-alumina (Aguadoet al., 1997)

The amorphous silica-alumina was prepared by the sol-gel route following a two-step method. In the first one, 16 g of tetraethyl orthosilicate was hydrolyzed with 10 g of 0.2 M aqueous HCl at room temperature for 45 min. Once the initially two-phase system became monophasic, a solution containing 0.523 g of aluminum isopropoxide in 7 g of isopropyl alcohol was added, and the mixture was stirred for 10 min to complete the hydrolysis of the Si and Al alkoxides. In the second step, the gel point was reached by drop-wise addition of 21 wt% aqueous ammonia solution. The cogel obtained was dried at 110 °C overnight and activated by calcination at 550 °C for 14 h.

Characterization of catalysts

The scanning electron microscopy (SEM-EDX) images were recorded on a JEOL-SEM, VERSION 3, 7600F, equipped with an energy-dispersive X-ray spectrometry detector at 5 kV. The BET-specific surface area and pore volume were determined by measuring nitrogen adsorption-desorption isotherms at liquid N_2 temperature (-196 °C) with a BELSORP MINI-11 (BEL Japan) apparatus. Belsorp Adsorption/Desorption Data Analysis Software-Ver. 6.1.0.8 was used to analyze and evaluate BET surface area and pore size distribution. Before each measurement, the samples were pretreated at 165 °C for 1.5 h under N_2 gas flow.

Characterization of liquid products

GC-MS, FTIR, and ^{1}H NMR spectroscopy analyzed the liquid products. For FTIR analysis, the Shimadzu 8400S, Japan, with KBr (heated at 100 ° C for 1 day before analysis) pellets in the 400-4000 cm^{-1} range were used. The Shimadzu GC-MS-TQ8040 with a quadrupole mass analyzer for GC-MS/MS analysis and electron impact ionization technique for MS detection (full scan mode 50-550 m/z) were used. A liquid sample of 0.5 μL was injected in splitless mode (flow rate of 1 mL/min and run time of 30 min) capillary column Rxi-5ms of 30 m length × 0.25 mm id at 250 ° C. The oven temperature was set to 50 ° C for 1 min and increased to 150 ° C at the rate of 5 ° C/min and then to 300 ° C at 15 ° C/min. Different compounds were identified using the computer-assisted mass spectral search by NIST-MS Library 2009. The^{1}H NMR of liquid products was conducted by the Bruker model (AVANCE III HD, 400 MHz).

Pyrolysis of waste high-density polyethylene (HDPE) and low-density polyethylene (LDPE)

The pyrolysis of waste HDPE and LDPE was investigated in a locally developed stainless steel reactor with a dimension of length, internal diameter, and outer diameter of 100, 75, and 77 mm, respectively (Fig. 1). The reactor consists of an electric furnace, thermocouple, temperature controller, condenser, and liquid collection vessel. 50.0 g of HDPE or LDPE were taken in each pyrolysis. In each catalytic pyrolysis experiment, a mixture of silica-alumina catalyst and HDPE or LDPE plastic (catalyst to plastics ratio 1:10, 1:15, and 1:25) was taken in the reactor and heated up to 450 °C under a nitrogen atmosphere. The reaction mixture was stirred by a mechanical stirrer. The condensable liquid products were collected through the condenser and weighed. The duration of each experiment was 30 min. Some coke was deposited on the catalysts after the completion of each catalytic reaction. Hence, each catalyst was used only once.

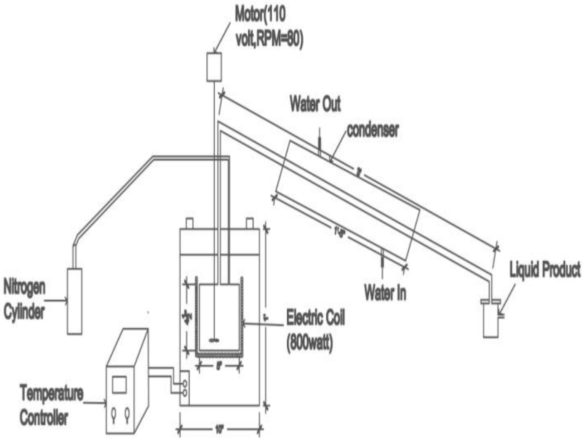

Fig. 1. Reactor setup for plastic pyrolysis

Results and discussion

The silica-alumina scanning electron micrograph (SEM) (Fig. 2) shows the morphological features. The micrographs indicate the disaggregation of the particles. The particle size is a few nanometers that are almost the same size. Fig. 3 displays an EDX spectrum for silica-alumina catalyst, and Table 1 shows silicon and oxygen are the most common elements making up the catalysts, with aluminum also being prevalent. The silica-alumina contained silicon and oxygen in SiO_4 tetrahedra, with a meager amount of aluminum. The Si/Al ratio of the silica-alumina is 98.5.

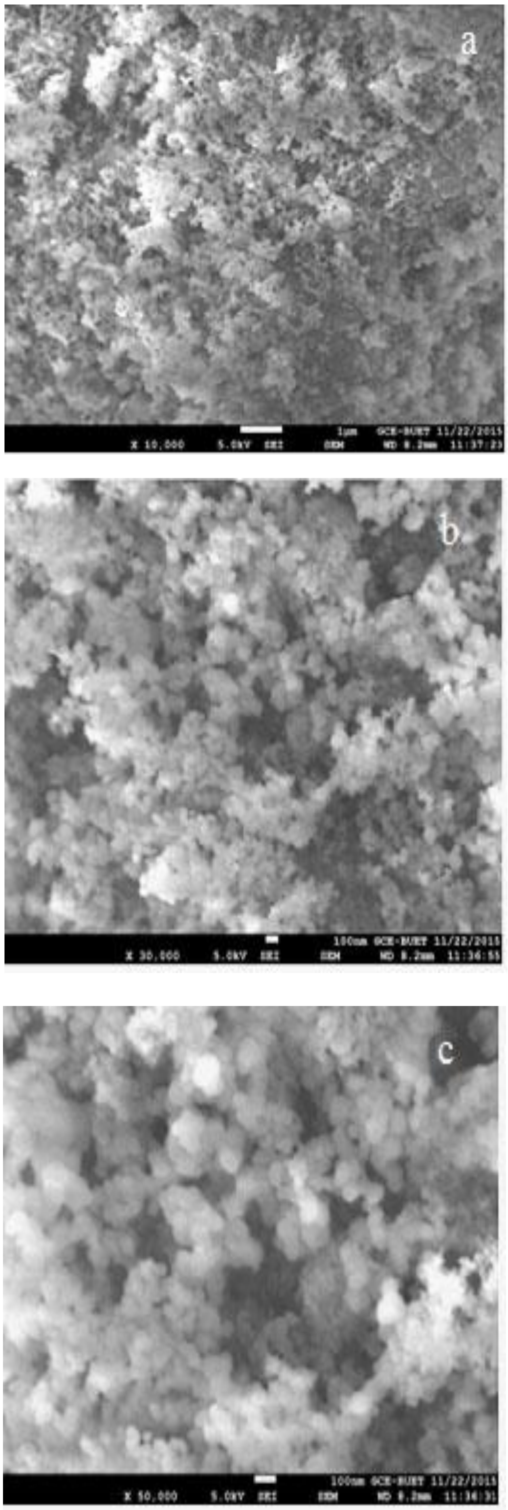

Fig. 2. SEM of silica-alumina (a) 10,000, (b) 30,000, and (c) 50,000 magnification.

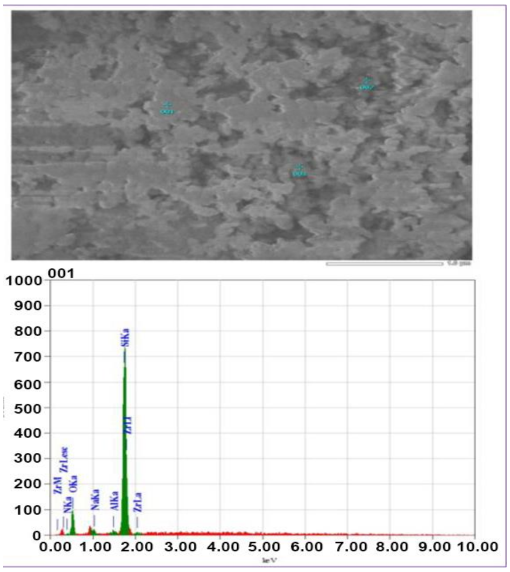

Fig. 3. EDX of silica-alumina

Table 1. Average weight % and atom % of each element in the catalyst sample

	N	O	Na	Al	Si	Zr	Si/Al
Atom%	4.51	31.71	0.60	0.63	62.06	0.49	98.5
Mass%	2.64	21.23	0.58	0.71	72.96	1.88	

The N_2 adsorption-desorption isotherms of the silica-alumina are shown in Fig. 4. The isotherms of these samples are classified as type IV based on IUPAC recommendations; this isotherm type is typical of mesoporous structures. The hysteresis loop of these samples is similar to type H3, typical of agglomerates of plate-like particles containing slit-shaped pores (Temuujin et al., 2001; Thommes, 2010). The isotherms also suggest the presence of some micro and macroporosity.

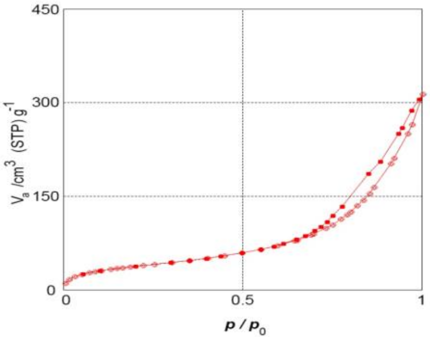

Fig. 4. N_2 adsorption/desorption isotherm of silica-alumina.

Table 2. Properties of $SiO_2 - Al_2O_3$ catalyst

Si/Al	BET			BJH		
	$a_{s'BET}$ $[m^2g^{-1}]$	T. Pore Vol.$[cm^3g^{-1}]$	Pore Dia.[nm]	V_p $[cm^3g^{-1}]$	Peak area[nm]	a_p $[m^2g^{-1}]$
98.5	1.4151E+02	0.4551	12.865	0.4832	4.03	181.95

BET= Brunauer-Emmett-Teller: BJH=Barrett-Jovner-Halenda

The BJH pore size distribution is given in Fig. 5, and pore volume and BET surface area are summarized in Table 2. It has been found that the BET surface area is 141.51 m^2g^{-1}, the mean pore diameter is 12.865 nm, and the total pore volume is $(p/p_0 = 0.990)$ 0.4551cm^3g^{-1} which is a typical feature of the uniform mesoporosity of this catalyst.

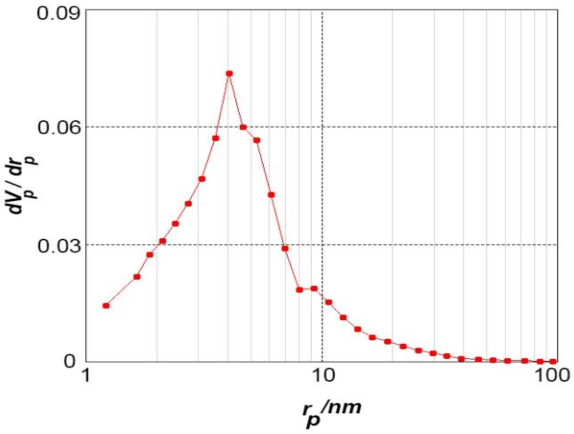

Fig. 5. BJH pore size distribution plot of silica-alumina

The amorphous SiO_2-Al_2O_3 exhibits a wide distribution of pore sizes. This material presents pores with sizes in the whole range between 1.3 and 40 nm, with two maxima around 4 and 9 nm, denoting the irregularity of its pore structure.

Catalytic pyrolysis of waste LDPE and HDPE using silica-alumina

As a control experiment, without any catalyst, the thermal pyrolysis of 50 g polyethylene provided 47% wax-like hydrocarbons at 485 °C. The wax was solidified at room temperature. In order to understand the effect of silica-alumina catalyst on pyrolysis ofboth single-used waste high-density polyethylene (HDPE) and low-density polyethylene (LDPE), we have carried out polyethylene pyrolysis at 450 °C inthe batch reactor under nitrogen atmosphere at various catalyst/plastic ratios of 1:10, 1:15 and 1:25. The gaseous hydrocarbon was vented off after pyrolysis and a small amount of coke was depositedonto the catalyst after pyrolysis. Hence, each catalyst was useda single time only. The durationof each experiment was 30 min. Table 3 summarizes the results obtained in the catalytic cracking of HDPE and LDPE over the silica-alumina catalyst.

Table 3. Pyrolysis of waste LDPE and HDPE using a silica-alumina catalyst. (450 °C, 30 min).

Catalyst	Plastics	Catalyst/Plastic ratio	Yield of liquid %
Silica-alumina	LDPE	1:10	70.56
		1:15	79.34
		1:25	87.69
Silica-alumina	HDPE	1:10	64.45
		1:15	75.67
		1:25	83.25

Table 3 shows that pyrolysis of LDPE at a catalyst-to-plastic ratio of 1:10 provided 70.56% liquid. An increased trend of liquid yield is observed with an increase in plastic ratio. For example, liquid yield increased from 79.34% to 87.69%, with the catalyst-to-plastic ratio increasing from 1:15 to 1:25 respectively. The liquid yield was higher in the pyrolysis of LDPE than HDPE. Similar to LDPE, an increased trend of liquid yield was observed with pyrolysis of HDPE. The pyrolysis of HDPE at a catalyst-to-plastic ratio of 1:10 provided 64.45%

liquid, which increased to 83.25% with the catalyst toplastic ratio of 1:25. Aguado et al., 1997 also found thatamorphous silica-alumina catalyst effectively produces liquid hydrocarbon from the pyrolysis of LDPE and HDPE. They pyrolyzed model virgin LDPE and HDPE pellets and obtained liquid hydrocarbons. The Si/Al of the catalyst was 35.6, and catalyst to plastic ratio was 1:36. Whereas, using ZSM-5 catalysts, they got 50% gaseous product from pyrolysis of both HDPE and LDPE (Aguado et al., 1997). Uddin et al. (1997) investigated the pyrolysis of HDPE and LDPE polyethylene using a silica-alumina catalyst. They achieved 80.2% liquid from LDPE and 77.4% from HDPE at 430 °C. FTIR, NMR, and GC-MS characterized the liquid product.

The FTIR spectrum of liquid obtained from pyrolysis of LDPE (Fig. 6) shows that the liquid contains linear alkanes and branched alkanes and alkenes. The observed peaks were assigned as follows: 2956 cm^{-1} C-H stretching of alkane; 1651cm^{-1} C=C stretching of alkene; 1458 cm^{-1} >CH_2 scissoring; 970 cm^{-1} C-H bending of alkane; 889 and 738 cm^{-1} C-H rocking from alkane. A similar FTIR spectrum was found in the liquid from pyrolysis of HDPE.

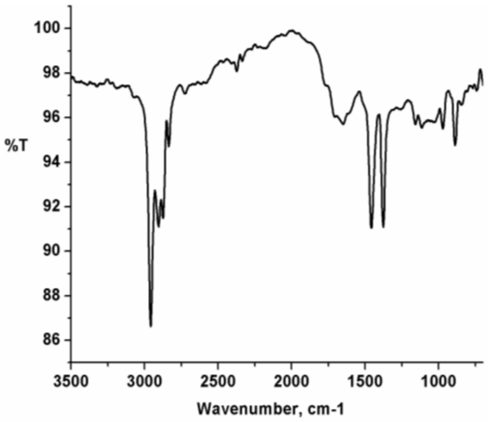

Fig. 6. FTIR spectrum of liquid obtained from pyrolysis of LDPE.

The ^1H NMR of liquid obtained from pyrolysis of LDPE (Fig. 7) shows peaks only in the range of 1-1.9ppm, which correspond to alkyl (methyl) and alkylene (methylene) protons originating from alkane compounds. A similar ^1H NMR spectrum was found in liquid from pyrolysis of HDPE.

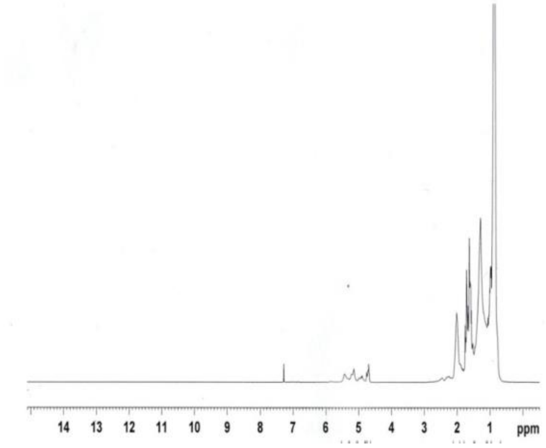

Fig. 7. The ^1H NMR of liquid obtained from pyrolysis of LDPE.

The GC-MS of the liquid was carried out to understand the composition of the liquid product.

Compounds were identified using the computer-assisted mass spectral search by NIST-MS Library 2009.The GC-MS of liquid obtained fromLDPE and HDPE (Tables 4 and 5) shows that the liquid contains mostly n-pentane, 2-methyl-2-pentene, 3-methyl-2-pentene, 2,4-dimethyl-1-pentene, 2,3-dimethyl-2-heptene, 2,2-dimethyl-3-heptene.

Conclusions

Catalytic pyrolysis of waste HDPE and LDPE was successfully carried out at 450 °C under N_2 atmosphere. The surface area of the silica-alumina catalyst is 141.51m^2g^{-1}, and the mean pore diameter is 12.865 nm. The synthesized silica-alumina is mesoporous and shows type IV isotherm. The hysteresis loop of the silica-alumina is type H3. More than 80% liquid yield was achieved using a silica-alumina catalyst. The highest liquid yield was obtained from LDPE (87.69%) than HDPE (83.25%) at a catalyst-plastic ratio of 1:25. The GC-MS and FTIR show that liquid product contains linear and branched alkanes and alkenes. The ^1H NMR shows that the liquid contains no carcinogenic compound like benzene.

Table 4. GC-MS of liquid obtained from waste LDPE by silica-alumina catalyst at 450 °C

Retention time (min.)	Compound	Chemical formula	Retention time (min.)	Compound	Chemical formula
1.550	2-methyl- Propene,	C_4H_8	5.106	2,3-Dimethyl-3-hexene	C_8H_{14}
1.721	n-Pentane	$n-C_5H_{12}$	5.197	2,3,3-Trimethyl-1,4-pentadiene	C_8H_{14}
1.7753	cis-2-Pentene	C_5H_{10}	5.272	3-Ethyl-2-hexene	C_8H_{16}
1.785	2-Methyl-2-butene	C_5H_{10}	5.363	2-Methyl-2-heptene	C_8H_{16}
1.924	cis-3-Methyl -2-pentene	C_6H_{12}	5.583	1,3-Dimethyl-1-cyclohexene	C_8H_{14}
1.967	2-Methylpentane	C_6H_{14}	5.652	3,3, 5-Trimethyl-1-hexene	C_9H_{18}
2.085	2-Methyl-1-pentene	C_6H_{12}	5.978	2,3,5-Trimethylhexane	C_9H_{20}
2.154	3-Methyl-2-pentene	C_6H_{12}	6.369	2,3-Dimethyl-2-heptene	C_9H_{18}
2.202	2-Methyl-2-pentene	C_6H_{12}	6.476	Cyclohexane	C_6H_{12}
2.298	cis-3-Methyl -2-pentene	C_6H_{12}	6.690	cis-2-Nonene	C_9H_{18}
2.389	2,3-Dimethyl-2-butene	C_6H_{12}	6.823	trans-2,2-Dimethyl-3-heptene	C_9H_{18}
2.438	1,3-Pentadiene	C_5H_8	6.930	trans-3-Nonene	C_9H_{18}
2.475	1,4-Hexadiene	C_6H_{10}	7.053	4-Ethyl-3-hep tene	C_9H_{18}
2.518	2,4-Dimethyl-1-pentene	C_7H_{14}	7.171	1,2,4-trimethylcyclohexane	C_9H_{18}
2.593	3,4-Dimethyl-2-pentene	C_7H_{14}	7.267	6-methyl-1-octene	C_9H_{18}
2.646	2,3-Dimethyl-1-pentene	C_7H_{14}	7.417	2,3-Dimethyl-3-heptene	C_9H_{18}
2.721	cis-4-Methyl-2-hexene	C_7H_{14}	7.604	2,6-Dimethyl-3-heptene	C_9H_{18}
2.978	2-Methyl-1-hexene	C_7H_{14}	7.920	5-Undecene	$C_{11}H_{22}$
3.208	cis-3-Methyl-3 -Hexene	C_7H_{14}	8.984	3-Methyl-4-undecene	$C_{12}H_{24}$
3.325	cis-3-Methyl-2 -Hexene	C_7H_{14}	10.541	2,4,6-Trimethyl-3-heptene	$C_{10}H_{20}$
3.290	2,3-Dimethyl-2-pentene	C_7H_{14}	11.049	cis-3-Decene	$C_{10}H_{20}$
3.951	2,3-Dimethyl-2-hexene	C_8H_{16}	11.733	cis-4-Decene	$C_{10}H_{20}$
4.080	2-Methyl-1-heptene	C_8H_{16}	12.825	2,6-Dimethyl-2-octene	$C_{10}H_{20}$
4.149	3-Methyl-3-heptene	C_8H_{16}	13.846	cis-5-Undecene	$C_{11}H_{22}$
4.224	4-Methyl-2-heptene	C_8H_{16}	14.402	2,3,6-Trimethyl-4-octene	$C_{11}H_{22}$
4.336	2,5-Dimethyl-2-hexene	C_8H_{16}	15.253	2,6-Dimethylnonane	$C_{11}H_{24}$
4.411	4-Methylheptane	C_8H_{18}	15.515	4-Methyl decane	$C_{11}H_{24}$
4.572	cis-2-Octene	C_8H_{16}	18.863	2,4-Dimethyl-2-decene	$C_{12}H_{24}$
4.652	3-Methyl-1,4-heptadiene	C_8H_{14}	19.788	1-Dodecene	$C_{12}H_{24}$
4.743	2,4-Dimethyl-1,3-pentadiene	C_7H_{12}	4.919	2,5-Dimethyl-2-hexene	C_8H_{14}

Table 5. GC-MS of liquid obtained from waste HDPE by silica-alumnia catalyst at 450 °C

Retention time (min.)	Composition	Chemical formula	Retention time (min.)	Composition	Chemical formula
1.550	2-methyl- Propene,	C_4H_8	5.053	3-Methyl-3-heptene	C_8H_{16}
1.721	n-Pentane	$n-C_5H_{12}$	5.106	4-Methyl-3-heptene	C_8H_{16}
1.753	2-Methyl-1-butene	C_5H_{10}	5.197	5,5-Dimethyl-1,3-hexadiene	C_8H_{14}
1.790	2-Methyl-1-butene	C_5H_{10}	5.272	cis-4-Octene	C_8H_{16}
1.924	1-Hexene	C_6H_{12}	5.363	2-Methyl-2-heptene	C_8H_{16}
1.972	2-Methyl-2-pentene	C_6H_{12}	5.583	1,3-Dimethyl-1-cyclohexene	C_8H_{14}
2.085	2-Methyl-1-pentene	C_6H_{12}	5.657	3,3,5-Trimethyl-1-hexene	C_9H_{18}
2.202	2,3-Dimethyl-2-butene	C_6H_{12}	5.738	2,6-Dimethyl-3-heptene	C_9H_{18}
2.256	cis-2-Hexene	C_6H_{12}	5.978	2,3,3-Trimethylhexane	C_9H_{20}
2.304	3-Methyl-2-pentene	C_6H_{12}	6.363	2,3-Dimethyl-3-heptene	C_9H_{18}
2.389	4-Methyl-trans-2-pentene	C_6H_{12}	6.465	n-Propylcyclohexane	C_9H_{18}
2.438	4-Methyl-1,3-pentadiene	C_6H_{10}	6.690	2,4-Dimethyl-1-heptene	C_9H_{18}
2.475	1,3-Hexadiene	C_6H_{10}	6.823	4-Ethyl-3-heptene	C_9H_{18}
2.518	2,4-Dimethyl-1-pentene	C_7H_{14}	6.930	cis-3-Nonene	C_9H_{18}
2.593	3,4-Dimethyl-2-pentene	C_7H_{14}	7.048	trans-3-Nonene	C_9H_{18}
2.651	3-Methyl-trans-3-hexene	C_7H_{14}	7.171	1,2,4-trimethylcyclohexane	C_9H_{18}
2.721	4-Methyl-2-hexene	C_7H_{14}	7.267	5-Methyl-1-heptane	$C_8H_{18}O$
2.892	5-Methyl-2-hexene	C_7H_{14}	7.604	2,6-Dimethyl-2-heptene	C_9H_{18}
2.983	2-Methyl-1-Hexene	C_7H_{14}	7.920	2-Nonene	C_9H_{18}
3.101	3-Methyl-2-Hexene	C_7H_{14}	8.198	4-Nonene	C_9H_{18}
3.149	cis-3-Heptene	C_7H_{14}	8.984	1,2,3-trimethyl-Cyclohexane	C_9H_{18}
3.208	2-Methyl-2-hexene	C_7H_{14}	9.097	2,3-Dimethyl-2-heptene	C_9H_{18}
3.325	3-Methyl-3-hexene	C_7H_{14}	9.166	2-Methyl-2-octene	C_9H_{18}
3.390	3,4-Dimethyl-2-pentene	C_7H_{14}	10.541	2,4,6-Trimethyl-3-heptene	$C_{10}H_{20}$
3.834	3-Ethyl-4-methyl-2-pentene	C_8H_{16}	11.054	cis-4-Decene	$C_{10}H_{20}$
3.957	2,3-Dimethyl-2-hexene	C_8H_{16}	11.193	3-Ethyl-2-methyl-2-heptene	$C_{10}H_{20}$
4.021	3, 5-Dimethyl-2-hexene	C_8H_{18}	11.536	trans-5-Decene	$C_{10}H_{20}$
4.085	2,5-Dimethyl-1-hexene	C_7H_{14}	11.701	trans-3-Decene	$C_{10}H_{20}$
4.154	3-Methyl-3-heptene	C_7H_{14}	12.054	2,6-Dimethyl-4-octene	$C_{10}H_{20}$
4.224	4-Methyl-2-heptene	C_8H_{16}	12.825	2,6-Dimethyl-2-octene	$C_{10}H_{20}$
4.277	cis-3-Octene	C_8H_{16}	13.242	cis-3-Decene	$C_{10}H_{20}$
4.336	2,5-Dimethyl-2-hexene	C_8H_{16}	14.119	Trans-2-Decene	$C_{10}H_{20}$
4.411	4-Methyl heptane	C_8H_{18}	15.515	2,4,4-Trimethyl-1-hexene	C_9H_{18}
4.577	3-Methyl-3-heptene	C_8H_{16}	18.687	2,4-Dimethyl-2-decene	$C_{12}H_{24}$
4.652	5-Methyl-2-heptene	C_8H_{16}	18.869	2,3, 7-Trimethyl-2-octene	$C_{11}H_{22}$
4.732	2-Methyl-2,4-hexadiene	C_7H_{14}	19.783	8-Methyl-3 undecene	$C_{12}H_{24}$

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