

Catalytic Conversion of Waste Low Density Polyethylene into Valuable Products

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Summary: Waste low density polyethylene (LDPE) from household and industries are recognized to be a major environmental problem. LDPE represent a source of energy and valuable chemical products. Waste LDPE were pyrolysed catalytically in a batch reactor under atmospheric pressure. Calcium carbide was used as a catalyst to explore its effect on pyrolysis product distribution. The effects of temperature, amount of catalyst and time on the yields of the pyrolysed products were investigated. The effect of catalyst on the liquid yield was also studied. The results demonstrate that the temperature has a promising effect on the yield; however, high temperature, as well as high catalyst loading, caused a decline in liquid yield. The liquid obtained from catalytic pyrolysis of polyethylene was characterized physically by Density, Specific gravity, API gravity, Viscosity, Kinematic viscosity, Aniline point, Flash point, Watson characterization constant, Freezing point, Diesel index, Refractive Index, Gross calorific value, Net calorific value and ASTM Distillation were determined according to IP and ASTM standard methods for determination of fuel values. Results from the physical analysis of the liquid fractions are comparable with the standards used (gasoline, kerosene and diesel fuel oil). Phenols and carbonyls were also quantitatively determined by spectrophotometric methods using folin-denis and phenyl hydrazine reagents, respectively. The components of different hydrocarbons in the oil mixture were separated by using column chromatography and fractional distillation.

Introduction

There are several methods for disposal of municipal and industrial LDPE wastes, *i.e.* landfill, incineration, true material recycling, and chemical recovery. Landfill treatment and incineration destruction are quite expensive and may raise problems with unacceptable emissions. True material recycling, *i.e.* to convert the waste material into useful products that can be reused, can significantly reduce the net cost of disposal. However, it is generally accepted that true material recovery is not a long-term solution to treat waste LDPE [1]. This recycled material will be again disposed after some time as a waste.

Uddin *et al.* [2], Sharratt *et al.* [3], Park *et al.* [4], Masuda *et al.* [5], McIntosh *et al.* [6], Kagayama *et al.* [7], and Kaminsky *et al.* [8], were investigated chemical recycling, through which plastics wastes can be converted into fuel oil and valuable chemicals. Thermal degradation and catalytic degradation of waste plastics are two kinds of chemical recycling processes. The main

drawbacks of thermal degradation are wide product distribution and requirement of high temperatures, typically more than 500 °C and even up to 900 °C. Since thermal degradation demands relatively high temperatures and its products require further processing for their quality to be upgraded, catalytic degradation of polymer waste offers considerable advantages. Catalytic pyrolysis gives a mean to solve these problems. Suitable catalysts have the ability to control both the product yield and product distribution from polymer degradation as well as to reduce significantly the reaction temperature. Luo *et al.* [9], studied catalytic degradation of polyethylene into liquid fuel in a powder-particle fluidized bed. The optimum temperature they used was comparatively high *i.e.*, 550 °C. Lee *et al.* [10], Dawood *et al.* [11], and Monos *et al.* [12], described the effects of catalysts on the catalytic degradation of plastic by contacting melted plastic with catalyst in fixed bed reactors. Zhang *et al.* [13], reported the current situation of recycling waste plastics and technology of converting waste plastics into oil.

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Koç *et al.* [14], worked on catalytic and thermal oxidative pyrolysis of LDPE in a continuous reactor system. LDPE was both decomposed thermally and catalytic in a continuous reactor *via* as an oxidative media in the temperature range of 400–500 C.

So as the studies reported in the literatures about waste LDPE, pyrolysis have been carried out in the presence of various expensive catalysts and derived oils of high boiling point range at comparatively high temperature.

The objective of the present catalytic study on waste LDPE was to derive oil in the boiling range of commercial fuel oil at relatively low temperature, where calcium carbide (CaC_2) was used as a catalyst. Calcium carbide consists of pi (π) electrons and at high temperature energies of pi (π) electron changes that increases the vibrational energies of carbon-carbon bond up to resonance and results in pyrolysis of polyethylene [15-17].

Results and Discussion

The weight loss versus temperature curve for thermal decomposition of polyethylene under a linear heating rate, Fig. 1 shows that the decomposition was

a single step process with offset and end temperature of 175.5 °C and 400 °C, respectively. The curve shows that maximum weight loss related to volatilization of hydrocarbons occurred at 400 °C. Total 99.98% weight changes occurred from 175.5 °C to 400 °C. The residue weight was 0.2% and was found constant upto 1000 °C. This indicates that certain amount of char like carbonaceous material is formed during the decomposition of polyethylene. Along with the volatilization process, other reactions like cracking of side chains from aromatic rings, isomerization and polycondensation also occur. Therefore it indicates that all volatile matter of polyethylene has been decomposed to volatile hydrocarbons [15-18].

Polyethylene sample was also pyrolysed at different temperatures. It can be seen from the resulting plot Fig. 2 that maximum conversion was obtained at 400 °C. At this temperature conversion into liquid oil product was $12.0 \pm 0.2\%$, while conversion into gaseous product was $13.36 \pm 0.32\%$. Total conversion at this temperature was $25.36 \pm 0.52\%$.

In order to investigate the optimum temperature for catalytic pyrolysis of polyethylene,

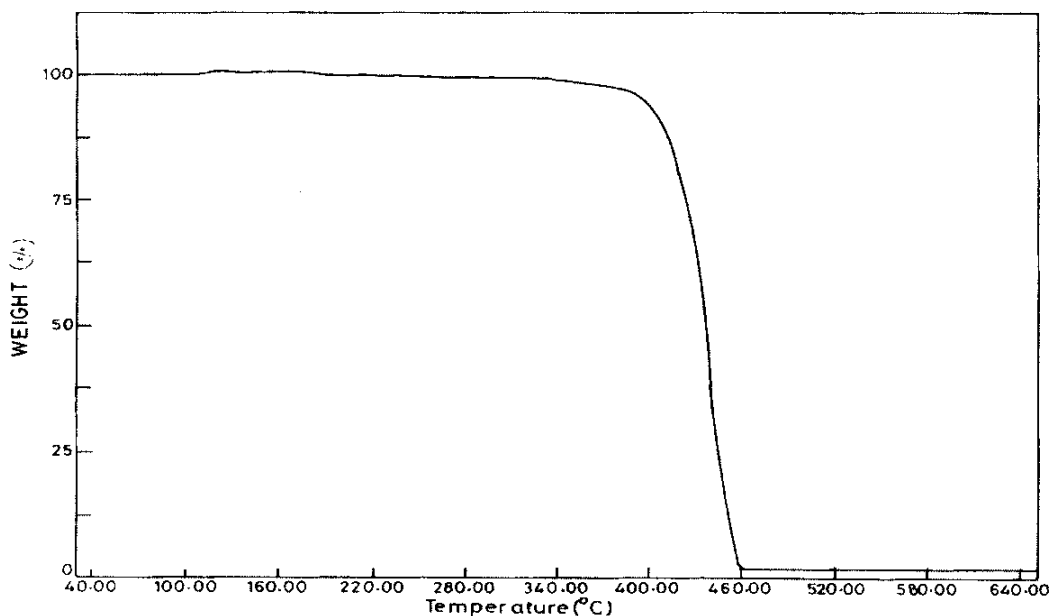


Fig. 1: TGA curve of waste LDPE.

polyethylene sample was catalytically pyrolysed at varied temperatures. The resulting plot is shown in Fig. 3. The product obtained was liquid oil, gases, and solid residue. The purpose of temperature optimization was to find out suitable temperature at which maximum liquid product could be obtained. Total conversion was based on the amount of liquid and gas formed during catalytic pyrolysis. It can be seen from the results that maximum conversion into liquid product 69.73% was achieved with this catalyst at 350°C. Beyond the optimum temperature a decrease in the liquid fraction was observed which could be due to further conversion into volatile product leading to higher fraction of gases and lower liquid fraction.

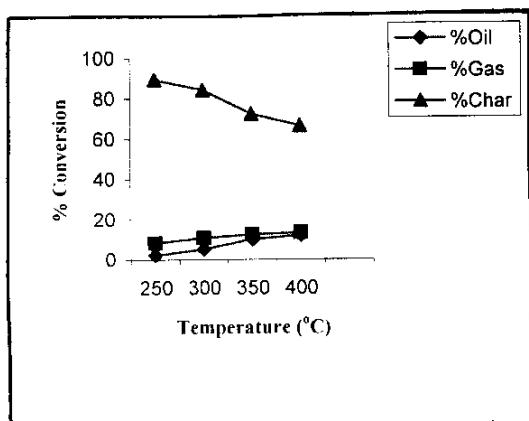


Fig. 2: Temperature optimization for pyrolysis of waste LDPE.

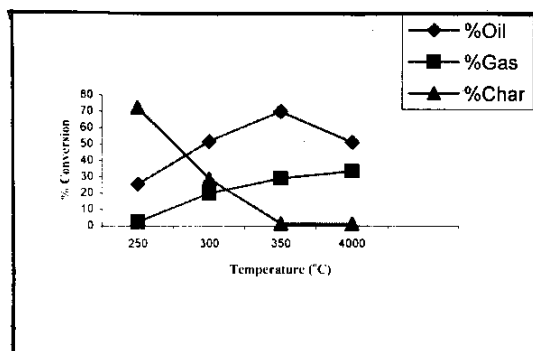


Fig. 3: Temperature optimization for catalytic pyrolysis of waste LDPE.

In the next step the effect of catalyst weight on the catalytic pyrolysis of polyethylene was

investigated in the range of 0 to 2.5 g at optimum temperature. The resulting plot is shown in Fig. 4. In the absence of catalyst the conversion into liquid was only 10.0%, while in the presence of catalyst the yield of liquid increased up to 69.73% with 1 g of catalyst (10%). So 1 g of catalyst weight (0.2 catalyst/feed ratio) was found as optimum catalyst weight for it. Below the optimum catalyst weight conversion into liquid oil was minimum, while higher weight of catalyst lead to higher gaseous product. This is due to the fact that at higher catalyst weight the rate of reaction increases the cracking process, which results in maximum gaseous product.

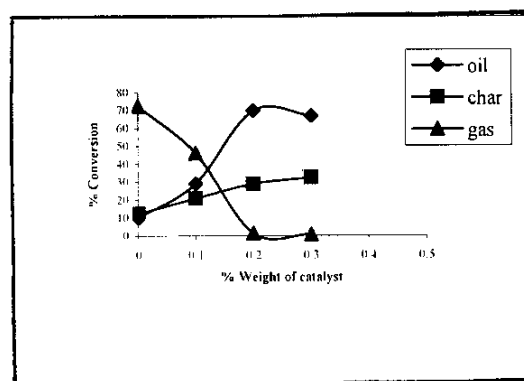


Fig. 4: Catalyst/feed ratio optimization for catalytic pyrolysis of waste LDPE.

The effect of residence time on the catalytic pyrolysis was also studied at optimum conditions of temperature and catalyst weight and the results are given resulting plot is shown in Fig. 5. It was investigated that 60 minutes reaction time sufficient for maximum conversion into liquid product. At this optimum time the conversion into liquid was 69.73%, which was the maximum conversion.

Liquid product at optimum conditions of temperature, catalyst weight and residence time was collected and analyzed for different fuel properties.

Characterization of Liquid Product

The liquid, usually termed oil is obtained in polyethylene catalytic pyrolysis. Separation of oil on silica gel column and analysis on GC were carried out with the aim to get an idea of the nature and type of compounds present in such oil. The sample was loaded on to the column and elution was done using

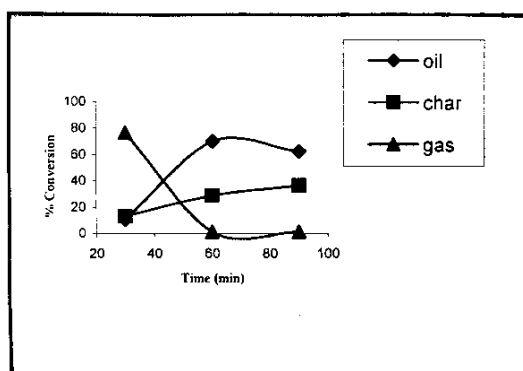


Fig. 5: Time optimization for Catalytic pyrolysis of waste LDPE.

different solvents like *n*-hexane, benzene and methanol. It was expected that aliphatic fraction will be eluted with *n*-hexane, aromatic with benzene and polar hydrocarbons with methanol. The results are given in Table-1. It can be seen from these results that the derived oil has maximum fraction of non-polar (40%) followed by relatively non-polar (30%) and minimum polar fraction (25%).

Table-1: Percentage of different fractions collected by column chromatography of waste LDPE using CaC_2 catalyst.

| S. No | Solvent system | % age of fraction |
|-------|------------------|-------------------|
| 1 | <i>n</i> -hexane | 40 |
| 2 | Benzene | 30 |
| 3 | Methanol | 25 |

The hydrocarbon groups of the derived oil having a boiling range of 80-217 °C were also separated into different boiling point range by fractional distillation. As can be seen from the Table-2, 15 wt% oil are below 170 °C and 40 wt% between

Table-2: Fractional distillation study waste LDPE using CaC_2 catalyst.

| S. No | Temp (°C) | % age of fraction |
|-------|-----------|-------------------|
| 1 | 80-170 | 15 |
| 2 | 170-250 | 40 |
| 3 | 250-300 | 13.33 |
| 6 | >300 | 30 |

Table-3: Physical parameters of various fractions collected at different temperatures from fractional distillation of waste LDPE oil.

| Temp (°C) | % | Density (g/mL) | Refractive index (n) | Refractive intercept (RI) | Refractive index Parameter (I) | Specific refraction (γ_D) |
|-----------|-------|----------------|--------------------------|---------------------------|--------------------------------|------------------------------------|
| 170 | 15 | 0.812 | 1.416 | 1.010 | 0.250 | 0.125 |
| 250 | 40 | 0.898 | 1.442 | 0.993 | 0.265 | 0.132 |
| 300 | 13.33 | 0.899 | 1.446 | 0.996 | 0.266 | 0.133 |
| Residue | 30 | 0.921 | 1.456 | 0.996 | 0.272 | 0.136 |
| Parent | 25 | 0.900 | 1.441 | 0.991 | 0.264 | 0.132 |

170-250 °C. This shows that maximum concentrations of hydrocarbons are within the range of initial boiling point 80-250 °C. The concentrations of hydrocarbons are 13.33 wt% and 30 wt% for boiling point in the range of 250-300 °C and greater than 300 °C, respectively. This indicated that major fraction of the oil contained components in the boiling point up to 300 °C which is the range of commercial petrol. All physical parameters like density, refractive index, refractive intercept, refractive index parameter and specific refraction for each fraction were also measured (Table-3). It can be seen from the results that the densities and refractive indexes of oil increased from 0.812 to 0.921 g/cm^3 and 1.416 to 1.456, respectively. There is pronounced increase in refractive indexes and densities with increasing boiling point of the fraction. At lower temperature low molecular weight hydrocarbons are present and with increase in boiling point the molecular weight of the compounds are also increased. Low values of refractive indices are associated with paraffins and higher values with aromatic and intermediate with naphthenic hydrocarbons. The nature of the hydrocarbon group present in each fraction was further identified from the refractivity intercept (RI) and it gives specific value for each hydrocarbon group. The RI value of paraffins lies in the range of 1.048-1.05, for naphthenic 1.03-1.046 and for aromatics 1.07-1.105 [14]. The RI values for fractions obtained in the boiling point range from 170-300 °C lie in between 0.993-1.010 which show the presence of naphthenic and paraffins hydrocarbons in the derived oil.

ASTM Distillation test at atmospheric pressure was carried out for the oils obtained at optimum conditions. The results are presented in Table-4. It was observed that 60% volume of such oils were easily distillable in boiling range between 80-20 °C which is the boiling point range specified for commercial petrol. On the other hand the remaining 40% volume of the oils has a boiling point under 217 °C, which is the boiling range for the 50% of distilled product in commercial kerosene oils.

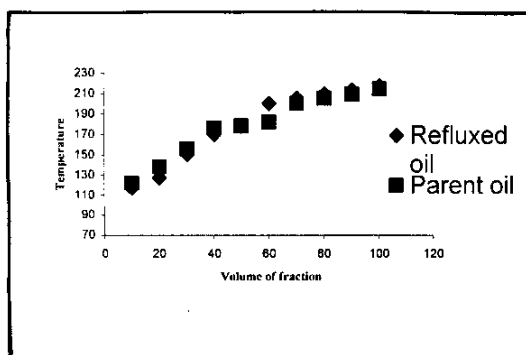


Fig.6: ASTM Distillation of waste LDPE.

Table-4: ASTM Distillation values for the Standards, gasoline, diesel and kerosene oil.

| S. NO | ASTM Distillation | Gasoline, Temp °C | Diesel, Temp °C | Kerosene, Temp °C |
|-------|-------------------|-------------------|-----------------|-------------------|
| 0 | Dew point | 49 | 120 | 110 |
| 1 | 10 mL | 69 | 225 | 178 |
| 2 | 20 mL | 78 | 238 | 180 |
| 3 | 30 mL | 82 | 252 | 180 |
| 4 | 40 mL | 86 | 272 | 182 |
| 5 | 50 mL | 90 | 281 | 190 |
| 6 | 60 mL | 94 | 290 | 192 |
| 7 | 70 mL | 98 | 299 | 198 |
| 8 | 80 mL | 102 | 300 | 200 |
| 9 | 90 mL | 106 | 301 | 210 |
| 10 | 100 mL | 112 | 305 | 220 |

Parent and Refluxed Oils

The oil obtained from catalytic pyrolysis with different catalysts without any further process has been named as parent oil. To find out that if there is any further cracking, each parent oil has been refluxed with its respective catalyst at temperature 350 °C for the time 2 h. The fuel properties like density, specific gravity, API gravity, viscosity, kinematic viscosity, aniline point, flash point, Watson characterization constant, freezing point, calorific

value, diesel index, sulfur and ASTM distillation for both the parent and refluxed oil in each case has been measured and compared with the standards, Kerosene and Gasoline oils

The results typical fuel properties are presented in Table-5. It can be seen from the physical properties that No considerable difference among the values of Density and Specific gravity is found for the parent and refluxed oil after reflux.

As a result of reflux, API gravity value shows slight increase for the refluxed oil from 52.93 to 53.12.

There is slight increase both in viscosity, (from 1.084 centipoises to 1.096 centipoises) and kinematic viscosity, (from 1.429 mm²/s to 1.432 mm²/s) upon refluxing with CaC₂ as a catalyst.

Slight decrease in aniline point, from 68 °C to 65 °C and slight increase in the flash point from 43 °C to 44 °C is observed on reflux.

No appreciable change in the Watson characterization constant values (12.163 and 12.179) were found for both parent and refluxed oil. From these values of Watson characterization constant, the oil may be considered aromatic and naphthenic in nature.

Slight change in the freezing point (-18 °C to -19 °C), gross calorific value (43.1 to 43.3 MJ/Kg) and net calorific values (41.2 to 41.5 MJ/Kg) is observed after reflux.

Diesel index value decreases from 81.719 to 79.144 while Sulfur content value shows slight difference, 0.68 to 0.69 %

Table-5: Typical properties of oil derived from catalytic pyrolysis of waste LDPE oil.

| S. No | Parameters | Parent Oil | Refluxed Oil | Gasoline | Kerosene |
|-------|--|------------|--------------|---------------|------------|
| 1 | Density (g/cm ³) | 0.759 | 0.765 | 0.736/0.725 | 0.780-0.82 |
| 2 | Specific gravity | 0.767 | 0.766 | 0.70 | 0.78 |
| 3 | API gravity | 52.93 | 53.12 | 65 | 41.7-39.66 |
| 4 | Viscosity (Centipois) | 1.084 | 1.096 | 0.7750-0.8394 | 0.9-1.5 |
| 6 | Kinematic viscosity (mm ² /s) | 1.429 | 1.432 | 5.0 | 2.2 |
| 7 | Aniline point °C | 68 | 65 | 65 | 62 |
| 8 | Flash point °C | 43 | 44 | 37.8-38 | 50-55 |
| 9 | Watson characterization constant | 12.163 | 12.179 | 12.45 | 12.126 |
| 10 | Freezing point | -18 | -19 | -58 | - |
| 11 | Gross calorific value (MJ/kg) | 43.1 | 43.3 | 83.44 | 59.88 |
| 12 | Net calorific value (MJ/kg) | 41.2 | 41.5 | 60 | - |
| 13 | Diesel index | 81.719 | 79.144 | 45.6 | 46.5 |
| 14 | % Sulfur | 0.68 | 0.69 | - | - |

The oxygenated compounds were determined quantitatively in terms of total phenols and carbonyls. It can be seen from the results (Table-6) that the parent oil with CaC_2 catalyst shows 8920 $\mu\text{g/mL}$ of total phenols and 123 $\mu\text{g/mL}$ of carbonyls. The presence of small concentration of phenols and carbonyls indicates that it may be due to the pyrolysis, cyclization and interaction of cracking product with atmospheric oxygen at high temperature in the presence of catalyst.

Table-6: Quantitative determination of total phenol and carbonyl compounds in the fractions collected at different temperatures of oil.

| Temp ($^{\circ}\text{C}$) | Phenol ($\mu\text{g/mL}$) | Carbonyl ($\mu\text{g/mL}$) |
|-----------------------------|-----------------------------|-------------------------------|
| 170 | 2400 | 35 |
| 250 | 1620 | 48 |
| 300 | 4450 | 20 |
| Residue | 450 | 19 |
| Parent | 8920 | 123 |

From the results for ASTM distillation, it can be seen that the initial boiling point is far beyond the initial point of gasoline which is 37-40 $^{\circ}\text{C}$ in summer grade gasoline oil. In some cases, the dew point is very high which indicates that the oil understudy mostly lie with in kerosene range.

Observed dew point of the refluxed oil is lesser than the parent oil. This shows that the catalytic activity of this catalyst might have cleaved heavy molecular weight configuration into light oil which cause initial boiling point to occur at temperature less than the parent oil. The final boiling point observed in the range of 217-214 $^{\circ}\text{C}$.

The interpretation of FT-IR spectra shows that catalytic pyrolysis of LDPE leads to the formation of a complex mixture of alkanes, alkenes, carbonyl group containing compounds like aldehydes, ketones, aromatic compounds and substituted aromatic compounds like phenols.

Above discussion shows that values for the fuel properties, (density, specific gravity, API gravity, flash point, gross calorific value and net calorific value), for both parent and refluxed oil fall in the range of Kerosene and Gasoline oil (Table-4).

Fuel properties like freezing point, viscosity and kinematic viscosity, final boiling point, for both falls in the range of Kerosene oil, whereas Aniline

point, Diesel index, Sulfur contents values are in good agreement with Gasoline oil.

Experimental

Material and Methodology

For the preparation of polyethylene representative sample, fine cuttings of transparent polyethylene shopping bags of 2 cm^2 area were cut with the help of scissor and used for analysis.

Thermogravimetric analysis of polyethylene sample was performed using a Perkin –Elmer TGA7 type instrument in which about 10 mg of sample was heated. The temperature was increased from 40 $^{\circ}\text{C}$ to final temperature of 1000 $^{\circ}\text{C}$ at a rate of

20 $^{\circ}\text{C}$ /minute. The sample temperature was measured with a thermocouple directly at the crucible very close to the sample.

For investigation of the optimum temperature for thermal analysis of polyethylene, five grams by weight fine cuttings of polyethylene sample were placed in pyrex glass tube and then heated in the heating assembly at atmospheric pressure, for 60 minutes at different temperatures *i.e.* 250 $^{\circ}\text{C}$, 300 $^{\circ}\text{C}$, 350 $^{\circ}\text{C}$ and 400 $^{\circ}\text{C}$. The cracking products at each temperature were collected and based on maximum conversion into liquid oil optimum temperature was determined.

For catalytic pyrolysis of polyethylene five gram of fine cutting of polyethylene sample of 2 cm^2 area and known amount of CaC_2 catalyst (100 μm mesh size) were mixed and added to the reaction assembly for the catalytic pyrolysis experiment. The pyrolysis experiments were carried out in a batch reactor under atmospheric pressure. A precisely weighed amount of both the sample and catalyst (Calcium Carbide) was loaded in a preweighed pyrex glass tube of 8.0 cm I.d. x 18 cm length, which was then put into the batch reactor. The reactor was heated with an electrical furnace. The temperature was measured by thermocouple and controlled by a temperature controller. The outlet of the glass tube was connected to trap in order to condense and weigh the liquid products. The glass tube was removed from the reactor at the end of catalytic pyrolysis and cool down to room temperature. The weight of solid residues could be measured by the weight difference

between glass tube with solid residue and empty glass tube. The weight of gaseous products could be calculated by subtracting the weight of liquid products and solid residues from the initial weight of waste polyethylene sample and the weight percentage of product composition could then be calculated.

Reflux Study of the Parent Oil Derived from Catalytic Pyrolysis of Polyethylene using Calcium Carbide as Catalyst

The parent oil product, 120 mL or which was obtained during the catalytic pyrolysis process, and 20 g of the CaC_2 catalyst were transferred to a pyrex glass tube and then the tube was inserted into the reactor, the temperature of the reactor was adjusted at 350°C and the mixture was refluxed for 2 hours. The refluxed oil was characterized using physical and chemical tests given below.

Determination of Physicochemical Properties of the Liquid Product

The liquid column chromatography was used to separate the different groups of hydrocarbons present in the derived oil. The silica gel 60 (63-200 μm grain size, supplied by Merck) was packed into borosilicate glass column and the pyrolysis oil applied to the top of the column. The column was then eluted with n-hexane, benzene and methanol to produce aliphatic, aromatic and polar fractions of the pyrolysis oil, respectively.

Fractional distillation was carried out to separate different boiling point hydrocarbon fractions from the liquid derived from catalytic pyrolysis of waste LDPE. The oil was distilled at a specific temperature until no more distilled products were collected.

The chromatographic analysis of each liquid fraction was carried out on a Shimadzu GC-14A equipped with a flame ionization detector. Separations were carried out on a fused-silica capillary column of 25 m x 0.53 mm i.d with film thickness of 0.15 μm . The temperature was programmed from 40 to 330°C at a rate of $5^\circ\text{C}/\text{min}$. The detector and injector temperature was 350°C and 300°C , respectively.

Infrared spectroscopy was used for identification of liquid product measuring absorption from 400 to 4400 cm^{-1} .

Phenols and carbonyls were quantitatively determined by spectrophotometric methods using folin-denis and phenyl hydrazine reagents, respectively.

The fractions obtained by this method were also characterized by using density, refractive index, refractive index parameter, (I) and refractivity intercepts (RI). The refractive indexes were calculated with Abbe's refractometer (P20-Warsaw, Poland) at 20°C . Refractive index parameter and refractivity intercepts were calculated for all the fractions by using the formulas:

$$\text{Refractive index parameter (I)} = \eta^2 - 1 / \eta^2 + 2$$

$$\text{Refractivity Intercept (RI)} = \eta - d/2$$

η = Refractive index, d = density.

Some physical properties of pyrolytic oils were determined by using the following standard methods: Flash point by Cleveland open cup method IP-36/84 and ASTM-D92-78. Density IP-59/82, API gravity IP-160/87 and ASTM-D1298-85, Kinematic viscosity IP-711/87 and ASTM-D445-87 and Distillation IP-191/83 and ASTM-D216-77 were determined according to IP and ASTM standard methods for fuel.

Gross calorific value was determined using Gallenkamp Auto Bomb Calorimeter (England).

Conclusion

It could be concluded, that catalytic pyrolysis of LDPE leads to the production of fuel oil, valuable resource recovery and reduction of waste problem. Catalytic pyrolysis of waste LDPE has also several advantages over other alternative recycling methods. It has been shown that the conversion at lower temperature in the presence of catalyst into liquid is a feasible process. An important difference is that the oil obtained relatively with greater volume and low boiling range in the presence of catalyst as compared to pyrolysis in the absence of catalyst. The total pyrolytic oil can be blended with the gasoline or kerosene. Consequently, evaluation of waste LDPE by catalytic pyrolysis is very important from economic and environmental point of view. However, further studies are necessary to utilize pyrolytic oil as liquid fuel or feedback.

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