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ORIGINAL RESEARCH

Conversion of waste plastics into low-emissive hydrocarbon fuels through catalytic depolymerization in a new laboratory scale batch reactor

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Abstract Pyrolysis of waste plastic is a prospective way of conversion of waste plastic into low-emissive hydrocarbon fuel. The present research is focused on the conversion of waste plastic into low-emissive hydrocarbon fuel by two process namely vacuum and catalytic cracking (activated carbon, activated carbon with granulated charcoal and activated carbon with calcium oxide). Waste plastic materials viz., polyethylene, polypropylene, polystyrene and polyethylene terephthalate were collected from local convenience store packing materials. Waste plastic material pyrolysis was conducted as individual plastics and as mixed feed in a new laboratory scale batch reactor. Hydrocarbon molecules from the basic materials are split under the impact of catalyst inside the reactor in 70–240 °C. The reduction of process takes place from 500–600 °C to 240 °C in the presence of catalyst. The analyses of pyrolysis products suggested that it can be used as a viable alternative to motor fuel. It was observed that the yield was better in the case of individual plastic material as opposed to mixed feed in all cases except polypropylene under non-catalysed vacuum process. The comparison of the GC-FID (TPH) report of the obtained oil with that of the commercial petrol clearly proves that the prepared oil is composed of petrol components.

Keywords Waste plastics · Pyrolysis · Alternative fuel · Catalytic conversion · Hydrocarbon · Petrol

Introduction

Due to the erratic change of energy prices and unfavourable forecast of world economy, considerable efforts have been devoted to substitute raw fossil fuels with various other sources for the production of energy. The various factors, such as ever increasing diesel consumption, large outflow of foreign exchange, and concern for environment, contribute to the search for a suitable environmental friendly alternative to fossil fuel. It is clearly envisaged that the increasing GDP and the limits of greenhouse gases can only be compensated by the application of waste recycling process (e.g., plastic, paper, metals, etc.) [1, 2]. The plastics have become one of the most important and indispensable materials in our contemporary world. These plastics are not presently biodegradable and are extremely troublesome components for land filling. The waste plastics are known for creating a very serious environmental challenge because of their huge quantities and the disposal problems caused by them [3]. To avoid the impact of the plastic in the environment, the recycling of plastics constitutes a valid alternative. Primarily, mechanical reprocessing is the method of plastic recycling which is the feasible only when high purity selectively collected wastes are available [4]. Alternatively, there is an attractive process for recycling by thermal or catalytic method which produces hydrocarbon. The pyrolysis can be cost effective compared to other processes.

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The pyrolysis thermally degrades the plastic component to produce an oil and gas product. This oil may be used as a liquid fuel or returned for refining [5, 6].

The pyrolysis has a wide temperature range and it can be performed with or without a catalyst. Generally used catalysts for this process are mordenite, FCC, USY, ZSM-5, etc. However, the addition of catalyst can be troublesome as the catalyst might get accumulated in the residue or coke [7–18]. Hence an alternative catalyst has to be introduced in the process, which must bring about a reduction in the energy consumption and an increase in the yield. Much research has been conducted on thermal cracking studies on polyethylene [20], polystyrene [21], and polypropylene [22] as individual feedstock for the pyrolysis process. On the other hand, only a few have worked on the thermal decomposition of the mixed feedstock containing polyethylene, polypropylene and polystyrene [19].

The aim of the present research is to investigate the waste plastic pyrolysis in the presence and absence of the catalysts such as activated carbon or calcium oxide to produce very low-emissive liquid hydrocarbon oil. The amount of waste plastic residue has to be reduced, with an increase in the efficiency of the fuel oils, thus providing an alternate energy resource to the environment. This would bring about a major reduction in the pollution caused due to landfills of plastic wastes and air pollution through the incineration of plastics.

Experimental

Materials

The waste plastics were collected from the various places across the neighbourhood. Namely, high-density polyethylene (HDPE) was collected in the form of garbage containers, low-density polyethylene (LDPE) as used low-grade plastic bags, polystyrene (PS) in the form of disposable cutlery, polypropylene (PP) as used waste plastic containers, and polyethylene terephthalate (PET) as used plastic bottles. The melt flow index (MFI) and the density of the raw materials are listed in Table 1. The waste plastic materials were shredded and thoroughly washed with tap water. This helps to increase the surface area of material in contact with catalyst during pyrolysis.

Catalyst

The catalyst influences not only the structure of the products, but also their yield. Hence the results of pyrolysis in the absence of catalyst were compared with results obtained by pyrolysis which was carried out in the presence of the catalyst viz. activated carbon, granulated charcoal and calcium oxide. Due to its high degree of micro porosity, just one gram of activated carbon has a surface area in excess of 500 m^2/g, as determined by nitrogen gas adsorption. Activated carbon was obtained from Merck, India. Granulated charcoal was produced from wood. Calcium oxide laboratory chemical was obtained from Qualigens Chemicals, India.

Pyrolysis process

The pyrolysis process is an advanced conversion technology that has the ability to produce a clean, high-calorific value fuel from a wide variety of biomass and waste streams. It is the thermo-chemical decomposition of organic material at elevated temperatures in the absence of oxygen. The pyrolysis provides various operational, environmental and economical advantages. Under pressure and heat, the long chain polymers of hydrogen, oxygen, and carbon decompose into short-chain petroleum hydrocarbons with a ceiling length of around 18 carbons. Hydrocarbon molecules from the basic materials are split under the impact of the catalytic (carbon material) convertor inside the reactor at 70–240 °C. The reduction of process temperature takes place from 500–600 °C to 240 °C. The higher yield of liquid fuel of about 98 % was achieved.

Distillation

The distillation is a method of separating mixtures based on differences in their volatilities. The collected oil from pyrolysis process was found to contain various percentages of gases and various densities of oil. The presence of the catalyst has enhanced the medium to reflux and then

Table 1 Melt flow index and the density of the raw materials

Waste polyolefin	Source	MFI (g/10 min)	Density
Polystyrene	Disposable cutlery	8.0	0.961
Polypropylene	Plastic containers	40.0	0.905
High-density polyethylene	Garbage containers	7.1	0.965
Low-density polyethylene	Plastic bags	70	0.910
Polyethylene terephthalate	Plastic bottles	8.5	1.38

distilled to obtain three fractions viz. gas, light oil, and heavy oil.

Regeneration of spent catalyst

The spent catalyst was first dissolved in some amount of water and heated to around 80 °C. The residue material was separated using Whatman no. 40 filter paper. The catalyst was then dried to about 80 °C using a heating oven. The regenerated catalyst was used for another batch operation.

Experimental setup

A wide range of reactors have been used on a laboratory scale for the plastic pyrolysis process. The reactor set-up in this research is a batch reactor. A common variant between the batch and semi-batch operations is the vacuum, which causes the reduction of temperature of the reaction to take place inside the Borosil round bottom flask. The two types of feed patterns were used, namely individual types of plastics and mixed types of plastics. The composition of the individual and mixed plastic wastes is given in Tables 2, 3, 4, 5 and 6.

The pre-processed waste plastic materials were transferred into an empty round bottom borosil glass flask of capacity 1000 mL. The empty weight of round bottom flask was found to be 343.12 g. After the raw materials were loaded into the round bottomed flask, the opening was connected to a condenser and the condenser was connected to a receiving adapter. The round bottom flask is fixed with heating mantle. The oil is collected at the bottom end. During the whole process, the temperature was maintained around 30 to 240 °C and a vacuum pressure of about 300 mm Hg maintained. A vacuum pump was used to create vacuum inside the round bottom flask. The temperature was raised according to the gradient. The experimental setup is shown in Fig. 1. The condensed oil was collected in the oil collector. The melting points of the various feed types with and without the catalysts are summarized in the Table 7. The collected oil was refluxed and further distilled. After distillation process, three types of fractions were obtained from the present research. The whole process of pyrolysis took place under 45 min to complete.

Table 2 Individual plastic for non-catalytic degradation process

Individual plastic materials	Weight in grams
Polyethylene	11.3
Polystyrene	15
Polypropylene	20.052

Table 3 Mixed plastics for non-catalytic degradation process

Mixed plastic composition	Weight in grams
Polystyrene	15.924
Polypropylene	15.312
Polyethylene	14.906

Table 4 Mixed plastics catalytic degradation process (activated carbon)

Mixed plastic composition	Weight in grams
Polystyrene	15.122
Polypropylene	15.012
Polyethylene	16.552

Table 5 Mixed plastic for catalytic degradation process (activated carbon + charcoal)

Mixed plastic composition	Weight in grams
Polystyrene	15.039
Polypropylene	15.021
Polyethylene	16.221

Table 6 Mixed plastic for catalytic degradation process (activated carbon + calcium oxide)

Mixed plastic composition	Weight in grams
Polystyrene	15.2
Polypropylene	15.03
Polyethylene	15.884
Polyethylene terephthalate	15.68

Analysis of products

The liquid products were analysed by gas chromatograph (TRACE GC) with a flame ionization detector. It was provided with a 50 m × 0.32 mm Rtx$^{®-1}$ (Cross bond 100 % Dimethyl-polysiloxane) column. To further narrow down the qualitative analysis, a GC-FID total petroleum hydrocarbons (TPH) was also used. Each fraction was also subjected to a separate analysis viz. flash point, fire point and density. The results observed for the prepared oil were compared with the GC-FID report of commercial petrol. The effect of temperature depends on the increase in the time taken for the pyrolysis process (see Fig. 2).

Results and discussion

The overall conversion and residue, along with the various other parameters such as temperature maintained, applied

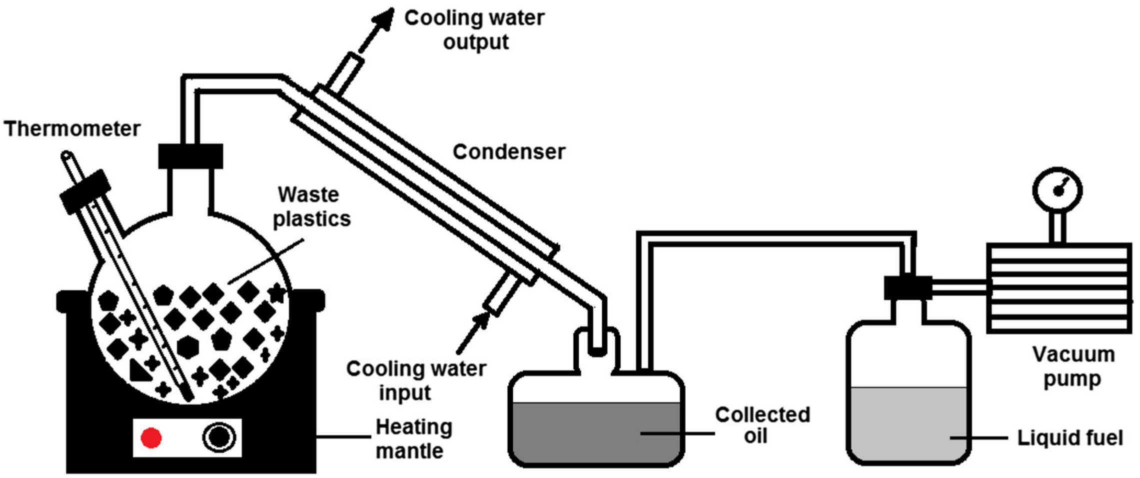

Fig. 1 Experimental setup

Table 7 Melting point of the various plastics and various processes

Raw materials	Catalysts	Melting point (°C)
Polystyrene	Nil	190
Polypropylene	Nil	120
Polyethylene	Nil	110
Mixed plastic	Nil	185
Mixed plastics	Activated carbon	75
Mixed plastics	Activated carbon + charcoal	75
Mixed plastics	Activated carbon + CaO	70

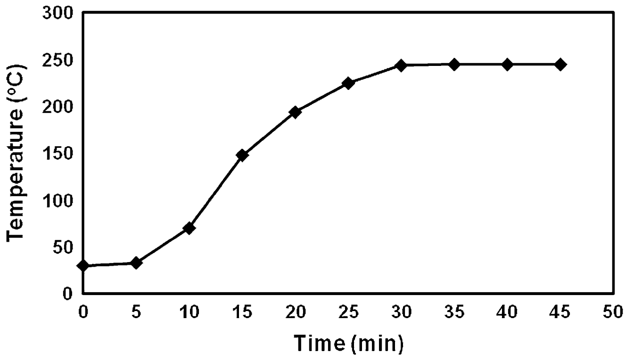

Fig. 2 Effect of contact time

vacuum pressure and the reaction time for the individual and mixed feed, are summarized in the Table 3. The various types of liquid hydrocarbon products were received from catalytic and non-catalytic cracking methods. The catalyst has influenced the yield and the composition of the liquid yield. The activity of charcoal has influenced the yield up to more than 95 %. The use of the calcium oxide along with the activated carbon was not proved to be much advantageous (see Table 8).

Physical properties of oil

Specific gravity and density

Hydrocarbons of low specific gravity can be calculated with the help of the ratio of maximum thermal energy to the volume of oil. The formula used for finding the specific gravity is given as:

$$\text{Specific gravity} = \frac{\text{density of sample}}{\text{density of water}} \quad (1)$$

A 10 mL specific gravity bottle was used to determine the specific gravity of the samples. 10 mL of the sample was pipette out into a pre-weighed bottle up to its brim. This gives the weight of the sample which when divided by 10 gives the specific gravity and hence the density of the sample can be found out. It was found to be having a specific gravity of 0.811 and a density of 811.7 kg/m^3.

Flash point

The flash point of a volatile material is the lowest temperature at which it can vaporize to form an ignitable mixture in air. The flash point is used to determine the (1) volatility of liquid fuels, (2) amount of low boiling fraction present in the liquid fuel, and (3) explosion hazards. The flash point of the sample was determined using Pensky Martens closed cup flash point test. About 30 mL of the sample was heated and stirred for every 1 °C rise in temperature. An ignition source is directed into the cup at regular intervals with intermittent stirring until a flash that spreads throughout the inside of the cup is seen. The corresponding temperature is known as the flash point and was found to be 65 °C.

Table 8 Experimental results of the process with and without catalyst

Plastic materials	Catalysts	Yield to liquid product (%)	Residue (%)	Temperature maintained (C)	Vacuum pressure applied (mm Hg)	Reaction time (min)
Polystyrene	No catalysts	80	13.33	240	−550	30
Polypropylene	No catalysts	60.7	34.40	240	−500	35
Polyethylene	No catalysts	75	22.43	240	−300	45
Mixed plastics (PE, PP, PS)	No catalysts	66.86	25.85	240	−350	45
Mixed plastics (PE, PP, PS)	Activated carbon	82.43	15.22	240	−300	45
Mixed plastics (PE, PP, PS)	Charcoal	95.54	2.33	240	−300	35
Mixed plastics (PE, PP, PS, PET)	CaO + activated carbon	75.50	20.33	240	−300	45

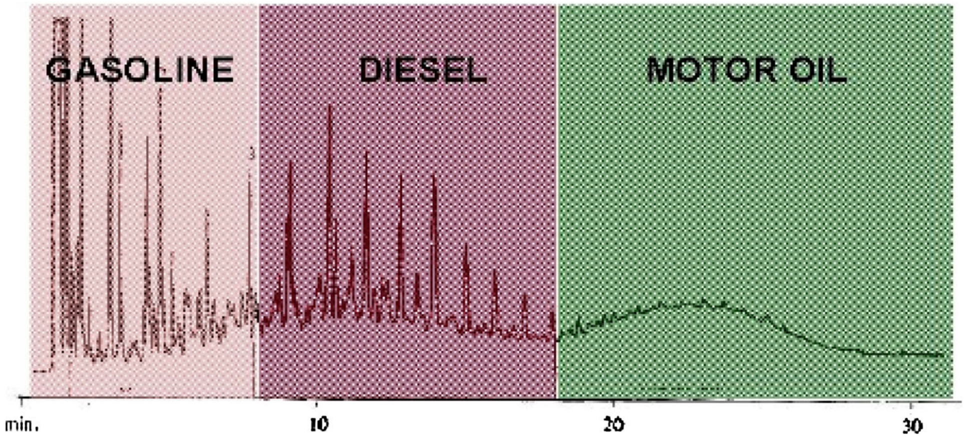

Fig. 3 GC-FID (TPH) report for petrol, diesel and motor oil

Fire point

It is the temperature at which the fuel will continue to burn for about 5 s after ignition by an open flame source. It is the temperature at which the vapour is produced to sustain a flame. The fire point was determined using the Pensky Martens open cup apparatus. About 30 mL of sample was heated and stirred continuously for every 1 °C rise in temperature. An ignition source was introduced into the cup at regular intervals until a flame sustains for at least 5 s. The fire point of the light fraction oil sample was about 110 °C.

Flame characteristics

The flame characteristics of the light fraction oil were studied and this was compared with kerosene and petrol. It was observed that there were no carbon settlements on the tiles. This suggests that the oil from pyrolysis process has similar characteristics of petrol. Henceforth, the chemical properties of the light fraction oil were checked by the GC-FID TPH analysis.

Gas chromatography (GC-FID TPH analysis)

Gas chromatography (GC) is the group of analytical separation techniques used to analyse volatile substances in the gas phase. Flame ionization detector (FID) is one of the most widely used detectors for GC. It has a wide field of application. For instance, the fuel for air planes, kerosene, is carefully analysed with GC-FID as a routine control. The overall complexity of the problem and of the spectrum of hydrocarbons is likely to be encountered. It is inevitable to view TPH as a single entity. This also relates to the sampling methodology employed. The approach consists of subdividing the hydrocarbon into the most volatile fraction (referred as gasoline range organics or GRO) and the less volatile less fraction. The GC-FID (TPH) for the petrol/diesel/motor oil and commercial petrol is shown in Figs. 3 and 4a, respectively.

The GC-FID (TPH) report for the oil, obtained as a result of pyrolysis, is shown in Fig. 4b. When the GC-FID (TPH) report of the obtained oil was compared with that of the commercial petrol, it was clearly evident that the prepared oil mainly consists of petrol components.

Conclusion

The current research process is technologically and economically viable for scaling up for industrial scale. There is no scarcity of feedstock as plastic waste generation has already become a habit of the modern society.

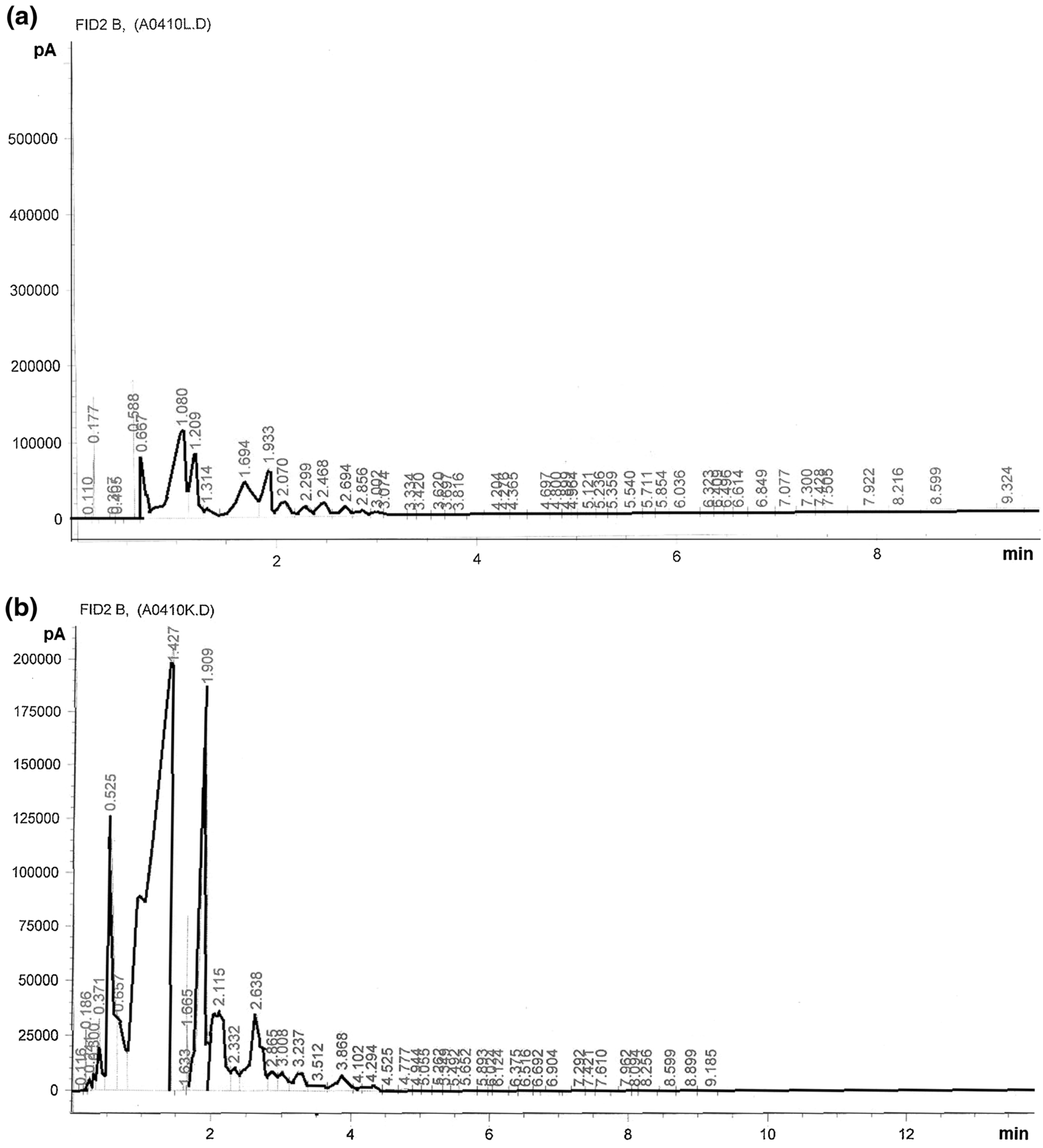

Fig. 4 **a** GC-FID(TPH) report for commercial petrol, **b** GC-FID(TPH) report for oil prepared from plastic wastes

- A simple catalytic and non-catalytic process for depolymerizing the waste plastics (individual and mixed plastics) to synthetic crude oil has been developed and further refined using a laboratory scale distillation followed by condensation process.
- The physical and chemical properties of the light fraction oil were done with the standard methods. The comparison of physical properties, chemical properties, and gas chromatograms suggests that the oil can be further fractionated and used as appropriate gasoline or aviation fuel.

- The characterization studies by GC-FID indicate that the depolymerization product is essentially all straight chain hydrocarbons when linear thermoplastic polymers are used as feed. GC-FID analysis indicates that the prepared oil includes hydrocarbons ranging from C_4 to C_{12}, a range that includes commercial gasoline. GC-FID analysis further indicates that the pyrolysed oil has higher percentage of petrol.
- The residue obtained from the distillation process can be used as lubricants for various types of equipment.

The present devised method may be an alternative method to recover higher amounts of oil from the waste plastic material.

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