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Conversion of low-density polyethylene plastic waste into valuable fuels using fly ash as a catalyst†

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Waste management of used plastic bags and fuel oil fly ash, which turn out to be one of the major causes of environmental pollution, is imperative to contribute toward sustainable development. In this study, waste low-density polyethylene (LDPE) plastic was pyrolyzed using a batch reactor along with a fuel oil fly ash catalyst, which is considered an efficient catalyst to transform heavy hydrocarbons into lighter hydrocarbons such as kerosene oil and diesel. A range of operating temperatures (450 °C, 500 °C, 550 °C, and 600 °C) and catalyst loadings (5%, 10%, 15%, and 20%) were investigated. Both aliphatic (saturated and unsaturated) and aromatic hydrocarbons were present in the oil product. The gross calorific value (GCV) of liquid oil was analyzed to assess the quality of fuel produced at different temperatures and catalyst loadings. The findings indicate that the conversion of this waste into oil through pyrolysis has the potential to be commercialized to address the environmental and energy crises. The liquid oil thus produced can be used for transportation fuel and industrial uses with minor post-processing and blending with conventional fuel such as diesel.

1. Introduction

Plastics have become an integral aspect of human existence, with their commercial utilization witnessing a significant surge in the last half-century. This substantial increase in plastic waste contributes to the mounting challenges of municipal waste management. The crux of the issue lies in the unpreparedness of the existing solid waste management system to cope with the evolving nature of our consumption patterns. Given that plastics are inherently non-biodegradable, owing to their production from fossil fuels, it becomes paramount to establish a resilient and sustainable plastic waste management solution.[1] With a strong focus on plastics, the European Commission is making decisive efforts to establish a circular economy that aims to facilitate the reuse, repurposing, and recycling of all types of plastic waste by the year 2030.[2] Under this agreement, the plastics industry is committed to operating through sustainable practices. Numerous alternative approaches exist for managing plastic waste and transforming it into a valuable resource. One such method is chemical recycling, wherein plastics are broken down into their elemental components and then reused to produce new products.[3] By employing this approach, it becomes possible to diminish the quantity of plastic waste that ultimately finds its way into landfills or the natural environment. Thermo-chemical conversion processes, like pyrolysis and gasification, offer efficient means of transforming organic wastes into valuable fuels. Additionally, other methods of managing plastic waste include biochemical recycling, biodegradation, and enzymatic degradation. Each of these processes comes with its unique set of advantages and disadvantages. The choice of appropriate alternatives hinges on various factors, including the type of feedstock, the desired end product, and the economic viability of the process. Researchers are continuously exploring different pathways to optimize these technologies, aiming to achieve efficient and cost-effective energy production through waste vaporization. Pyrolysis proves to be a highly effective thermo-chemical conversion process, enabling the transformation of waste plastics into valuable fuels and chemicals. This method entails heating the feedstock in the absence of oxygen, causing it to break down into its constituent materials. The output typically comprises a mixture of liquid, gas, and solid materials that can be utilized for the production of fuels or a wide array of chemicals. One of the key advantages of pyrolysis is its capacity to produce premium-quality fuel along with valuable by-products that find applications in both industrial and residential settings.[4] The composition and yield of these oil products are influenced by several factors, such as the type of plastic, temperature, heating rate, reactor type, and the presence of

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a catalyst or inert gas. For example, during pyrolysis, low-density polyethylene (LDPE) yields more gas compared to high-density polyethylene (HDPE), while polypropylene (PP) typically results in a higher amount of liquid product.[5] Catalytic pyrolysis is recognized as a potent method for achieving the desired product during the pyrolysis of plastic and biomass feedstock. HZSM-5,[6] FCC,[7] ZSM-5,[8,9] spent FCC,[10] Zeolite-β,[11] CoMo/Z,[12] Cu–Al_2O_3 (ref. 13), natural zeolite NZ,[14] $Al(OH)_3$ $Ca(OH)_2$ (ref. 15), red mud,[16] Fe_2O_3 (ref. 17) and activated carbons are crucial catalysts that have undergone testing in catalytic pyrolysis processes involving coal or waste plastic.[18] Nevertheless, the rapid deactivation and the expensive nature of commercial catalysts make the catalytic pyrolysis of waste plastic financially unviable on a large scale.[19,20] Exploring cost-effective alternatives that exhibit high performance could be a compelling endeavor in such pyrolysis processes. Fly ash, comprising SiO_2, Al_2O_3, and minor metal oxides like Fe_2O_3, TiO_2, CaO, MgO, K_2O, and Na_2O, represents a potential candidate for consideration.

The composition of fly ash closely resembles that of commercial and natural zeolites and metal oxide catalysts, making it a promising candidate as an alternative to commercial catalysts. Specifically, Fe_2O_3 has the ability to break down large hydrocarbon chains into smaller ones.[17] Additionally, the presence of unburned carbon in fly ash can also serve as a catalyst, facilitating the conversion of heavy hydrocarbons into alkanes[18] Moreover, fly ash contains activated carbon, a porous form of carbon treated with oxygen to enhance its pore structure and surface area, which can also function as a favorable catalyst to attain the desired hydrocarbon range for kerosene fuel. It has been projected that global ash production will reach approximately 430 million tons in the early 21st century, posing potential environmental challenges in its management.[21] The application of fly ash as a catalyst in pyrolysis reactions presents a viable solution to address fly ash management issues and fosters the progress of a circular economy and sustainable development.[22–24]

Several studies have indicated the effectiveness of fly ash-derived zeolites and amorphous silica-alumina catalysts in the pyrolysis of low-density polyethylene and polypropylene.[25] According to reports, amorphous silica-alumina obtained from fly ash proves to be a highly efficient catalyst for low-density polyethylene pyrolysis.[26] Activating fly ash with 3 M NaOH or 3 M H_2SO_4 was found to be effective as well for pyrolysis applications. Furthermore, researchers have discovered that fly ash can be used as a catalyst for the pyrolysis of LDPE and polypropylene.[27,28] Mondal *et al.*[29] used coal fly ash in pyrolysis of waste plastic and used a 25% ratio of coal fly ash and found 96% conversion. Similarly, Misran *et al.*[30] used coal fly ash as a catalyst in pyrolysis of plastics as well. Cocchi *et al.*[31] used coal fly ash as a catalyst in the hydrothermal process to liquefy plastic. During the co-pyrolysis of waste plastic and waste tires, Dutta *et al.*[32] utilized coal fly ash and observed a significant enhancement in the alkane percentage.

This study aims to transform waste plastics into value-added products by employing fuel oil-fly ash as a catalyst. Furthermore, it is the first investigation to explore the impact of fuel oil fly ash on product yield and quality during the catalytic pyrolysis of LDPE waste. In earlier studies, coal-fly ash was utilized in pyrolysis after undergoing treatment with an acid or alkali.[33] However, in the current study, the fuel oil fly ash was simply rinsed with deionized water, dried in an oven at 110 °C to eliminate moisture, and then employed in catalytic pyrolysis. The experiments were conducted using a large-scale batch reactor to yield significant outcomes, thereby facilitating the potential commercialization of plastic catalytic pyrolysis. Pyrolysis oil and other resulting products were collected and analyzed.

2. Materials and methods

2.1 Raw materials

Waste LDPE plastic was collected from a municipal solid waste stream of Wah Cantt City, Pakistan. LDPE waste feedstock was cleaned and dried to remove any extraneous material that may affect the experiment. Drying in open air followed by oven drying is intended to remove all moisture from the plastic waste feedstock. The shredding of the plastic waste feedstock into small pieces was performed to obtain a uniform average size of about 4 cm, which is important for conducting the experiments under controlled conditions.

The fuel oil fly ash was obtained from the Saba power plant in Punjab, Pakistan, which generates 134 MW h^{-1} by consuming 30 tons h^{-1} fuel oil. An electrostatic precipitator is installed which captures circa 8.6 tons of fly ash each month after an air preheater. In the absence of a suitable alternative utilization approach, fly ash is currently disposed of into a landfill. Before fly ash utilization in pyrolysis, fly ash was rinsed with deionized water to elute the sulfur compound which can, otherwise, be harmful to the environment and human health. Multiple rinsing cycles with deionized water were performed until pH reached 5.6. This reflects that the sulfur compounds have not been completely neutralized or removed from the fly ash. Thereafter, fly ash was dried at room temperature for one day followed by heating in an oven at 110 °C for 1 h to remove the moisture content. Overall, the preparation steps for both fly ash and plastic waste feedstock seem reasonable and necessary for ensuring that the experimental results are accurate and reliable.

2.2 Pyrolysis setup and experimental procedure

A pyrolysis reactor setup was designed and fabricated locally as shown in Fig. 1. The reactor setup consists of a central reactor with 4.8 liters capacity which is made of high carbon steel and is placed in an electric heater furnace. The reactor is equipped with a safety valve, inlet, and outlet valve, PID controller, and pressure gauge for process parameters monitoring and control. A nitrogen cylinder is connected *via* the bottom valve of the reactor for the initially purging of N_2 gas in the reactor and as a sweep gas during the process. A coil-type condenser made of a copper tube is installed at the outlet of the reactor.

For the detailed study of pyrolysis, the experiment was conducted at different temperatures of 450 °C, 500 °C, 550 °C, and 600 °C. For each pyrolysis experiment, 500 g of shredded polythene sample was loaded in the reactor. Initially, the reactor was

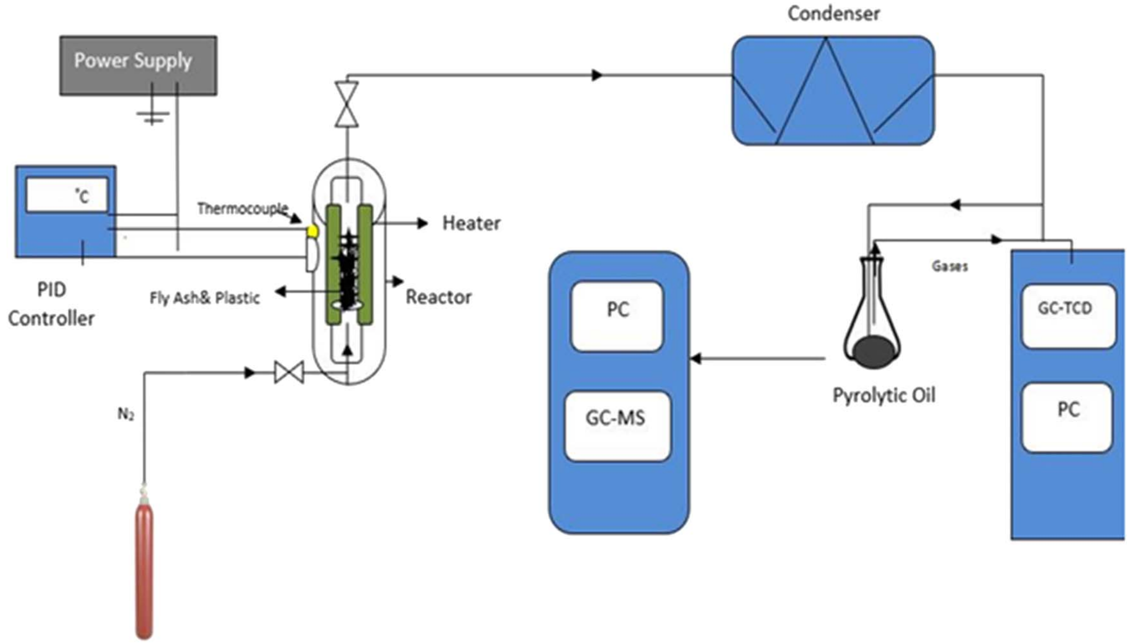

Fig. 1 Schematic diagram representing the pyrolysis setup.

purged with nitrogen gas at a flow rate of 330 ml min^{-1} for 15 minutes and then the flow was maintained at 55 ml min^{-1} during the reaction. The heating rate for the reactor was 12 °C min^{-1} to achieve target temperatures of 450 °C, 500 °C, 550 °C, and 600 °C. The liquid products were condensed through a condenser. Non-condensable gas samples were collected in bags. For each experiment, the reaction time was 65 minutes. The *in situ* catalytic pyrolysis of the reactants with the fuel fly ash catalyst was conducted in a reactor to save the energy and overall cost of the process.[34] All the catalytic experiments were performed at a temperature of 500 °C, which is found to be optimum temperature that resulted in maximum oil yield during thermal pyrolysis without a catalyst.[35] Different ratios of the fly ash catalyst (5%, 10%, 15%, and 20%) were used to determine its effect on the pyrolysis process. The solid and liquid products were weighed and subtracted from the initial weight of the polythene samples to calculate the mass of the gas product using a mass balance equation. Furthermore, it is important to ensure that the experimental setup and procedures are carefully controlled and documented to ensure the accuracy and reliability of the results. The physical and chemical characteristics were determined through various analytical techniques *inter alia* a flash point, viscometer, NMR, GCMS, and GCV of products.

2.3 Feedstock and catalyst analysis

The feedstock for pyrolysis was characterized by proximate analysis to find volatile and nonvolatile components. Proximate analysis is a method of analyzing the composition of a substance by dividing it into its primary components. In the case of waste polyethylene, proximate analysis can be used to determine the volatile and nonvolatile components of the feedstock, which can be useful in the pyrolysis process. ASTM D3172-75 is a standard test method for proximate analysis of coal and coke, but it can also be used for the analysis of other solid fuels, such as waste polyethylene. By measuring the percentage of each component, proximate analysis can provide an estimate of the fuel's heating value, combustion properties, and potential for pyrolysis.

The fuel fly ash catalyst was analyzed though SEM, EDS and FTIR to assess the surface morphology, elemental composition, and presence of various functional groups respectively. Moreover, the surface area of the catalyst was determined using the BET method. The pH of fly ash was also tested with a pH meter before and after rinsing with deionized water. To measure the pH, fly ash was dissolved in deionized water and agitated at 150 rpm for 1 hour to create a uniform suspension.[36] Subsequently, the pH was determined using a digital pH meter (HQ-4110) at the Saba power plant laboratory.

2.4 Analysis of pyrolysis products

For elemental analysis of the char product, samples were collected and analyzed using the CHNS/O standard analytical technique using a 5ECHN 2200 model CKIC analyzer. Approximately, 80 mg of each sample was used in the analyzer during analysis. Furthermore, the sulphur content of char was determined by adopting the CHN analyzer procedure *via* a 5EIRS II model CKIC sulphur analyzer with 300 mg of sample.

Then the liquid products were analyzed for gross calorific value (GCV) values using a Parr-6200 isoperibol bomb calorimeter. The standard method of ASTM D240-02 was followed. Each sample of 0.5 g was placed in a crucible and fed into a vessel and oxygen was filled in the vessel. After filling the oxygen in the vessel, the ignition started to burn the sample. The GCV was calculated after burning the sample and comparing it with the calibrant.

A DV2T touch screen viscometer-AMETEK Brookfield is used for measuring the viscosity of the obtained liquid product. To perform viscosity measurements, a sample of the liquid product (in this case, 17 ml) is placed in a vessel and connected to a spindle. The spindle is then rotated at 25 rpm while the viscosity of the sample is measured. The temperature of the sample is also controlled and set at 40 °C. By measuring the viscosity of the liquid product, we can gain insight into its flow behavior and potential uses. For example, a high viscosity product may be more suitable for use as a lubricant or coating, while a low viscosity product may be better suited for use as a solvent or cleaner. Overall, viscosity measurements can provide valuable information for product development and quality control.

By following the standard procedure of ASTM D93-18 and using a Koehler K16225 Pensky–Martens Closed-Cup flash point tester, the flash point of a liquid product was determined with a high degree of accuracy and reproducibility.

GC/TCD analysis was performed to check the chemical composition of the gases. The composition of the permanent gases (H_2 and CH_4) was determined by using a Thermo Scientific TRACE Ultra GC, coupled with a thermal conductivity detector (TCD). The column used for gas composition assessment was a CARBOXEN 1010 PLOT packed with silica and helium as the carrier gas. The GC oven temperature was maintained at 40 °C for 7.5 min, programmed to reach 200 °C at a rate of 50 °C min^{-1}, and held there for a further 10 min.

The chemical compositions of the recovered liquid oil were analyzed by using an Agilent 7890A GC-MS (GC-MS; GC, Agilent 7890A; MS, Agilent 5975C) with a DB-5 capillary column. Before this process liquid oil was diluted with *n*-hexane and the obtained solution samples were used for analysis. The GC was first programmed for heating to 50 °C for 5 min followed by heating to 300 °C for 5 min at a rate of 10 °C min^{-1}. A sample of 1 μl was injected. The helium gas was used as the carrier gas with a 0.6 ml m^{-1} flow rate. The ion source temperature was 230 °C for the mass selective detector. The NIST library spectral data were used to identify the compounds. The area percent of compounds obtained from GC/MS results was utilized for quantitative analysis of a certain compound with various concentrations and was also analyzed by the same procedure. The data thus obtained were used to calculate the absolute concentration of compounds in liquid fuel. Likewise, the functional groups of liquid products were determined by using a Bruker Alpha model.

The aliphatic and aromatic compounds were determined by NMR (Avance series, Switzerland). NMR at a resonant frequency of 75 MHz was used to determine the aliphatic and aromatic compounds in the liquid sample. Samples were pretreated with a nylon microfilters prior to NMR analysis. The information about aromatic and aliphatic compounds of the liquid oil sample was recorded and analyzed.

3. Results and discussion

3.1 Feedstock characterization

Table 1 Comparison of proximate analysis of waste plastic used in this study with waste plastic reported in relevant literature

Moisture (%)	Volatile matter (%)	Ash (%)	Fixed carbon (%)	Reference
0.0	82.6	5.8	11.6	This work
0.0	82	4	14	37
0.41	96.88	2.43	0.28	38

Proximate analysis of waste LDPE feedstock revealed that 82.6% volatile matter, 5.8% ash, and 11.6% fixed carbon (Table 1) are present. These results are comparable with the findings of other reported studies where ash matter 4%, volatile matter 82% and fix carbon 14% are reported.[37] According to the proximate analysis of waste plastic in other relevant studies, the volatile matter is 96.83%, ash content is 2.43% and fixed carbon is 0.28%.[38] The product yield of the pyrolysis process depends upon the proximate analysis of waste plastic. The 82.6% highly volatile matter in waste plastic confirms that waste plastic is potential feedstock for the production of high-quality oil through the pyrolysis process.

3.2 Characterization of the fly ash catalyst

The pH of the fuel oil fly ash was assessed both before and after rinsing with deionized water, resulting in pH values of 3.8 and 5.6, respectively. Multiple rinsing cycles were conducted until the pH stabilized at 5.6, indicating that the sulfur content in the fuel oil fly ash could not be further removed with water, leading to its persistent acidic nature. In order to identify the morphology, SEM is one of the most widely used techniques. Fig. 2a and b show the SEM image of the fly ash sample giving indication of the presence of numerous spherical particles having irregular shapes. The rounded particles with a wide distribution in size mostly comprise crystalline solids. Moreover, it can be observed that macro- and micro-pores are present in the catalyst reflecting the high surface area for catalytic reactions. Macrospores work as conduits for pyrolysis volatiles during pyrolysis to enter into fly ash and then in microcavities where catalytic reactions are to be performed. Macropores provided the space to enter the long chain hydrocarbon into the catalyst cavities. Some primary reactions took place here to break the long chain hydrocarbons into shorter chains prior to entering into micropores.[39]

EDS surface element analysis was performed to determine the element distribution of fuel oil fly ash. The selected spots of the surface mainly contain C, Fe, Mg, and S. These elements are usually present in crude oil. It has been reported that Fe and Mg break the long chain molecules into short chains during the pyrolysis reactions.[40] Fly ash has numerous active sites for oxidation and cracking reactions due to its pozzolanic properties. Fly ash contains S and Sn that are usually helpful in breaking of bonds.[41,42] The elemental composition of fuel oil-fly ash has been assessed through EDX analysis, which is presented in Table 2. Based on the EDX analysis, Table 2 illustrates the elemental compounds found in fly ash, which are most likely oxides of the corresponding metals. Fly ash exists in the oxide form due to the combustion of mineral matter in

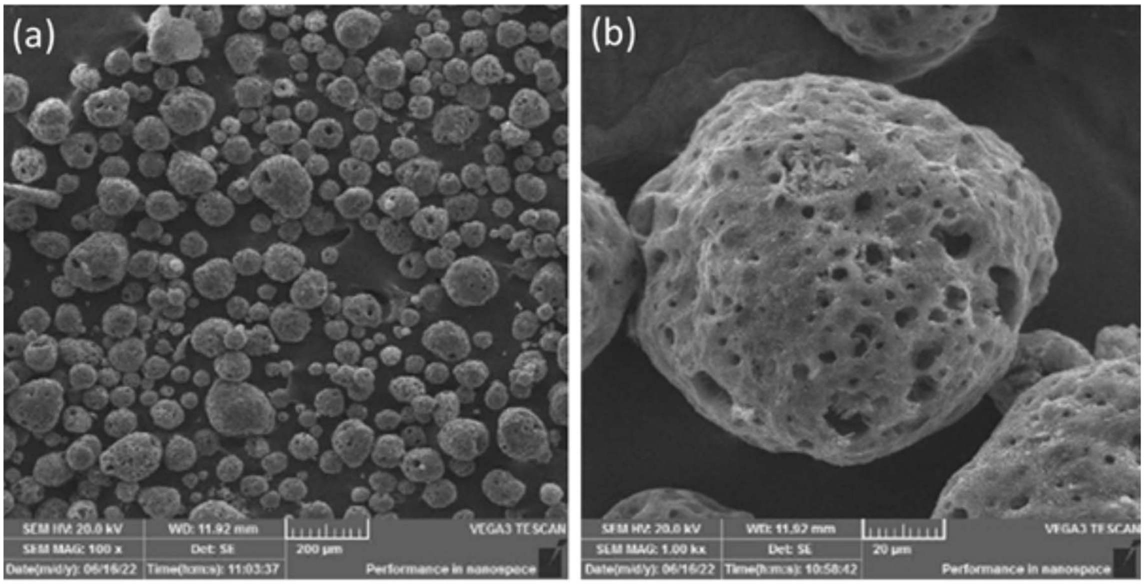

Fig. 2 SEM images of fly ash used as a catalyst in pyrolysis of LDPE (a) low magnification (b) high magnification.

Table 2 EDS elemental analysis of the fly ash catalyst

Element	Weight (%)
C	82.00
Fe	0.90
O	12.50
Mg	2.10
Sn	1.00
S	1.50

combustion facilities, as previously reported in the literature.[43,44]

FTIR was used to investigate the functional groups on the surfaces of fuel fly ash and the results are depicted in Fig. 3. These fly ash peaks, which represent –OH, S–H, C–H, C=O, and S–O at a wavelength of 3449, 2556, 1659, 1941, and 644, provided catalytic sites during the thermal pyrolysis of LDPE that promoted the cracking of C–C and C–H bonds of waste polythene bags, which increase the yield of alkenes.[39]

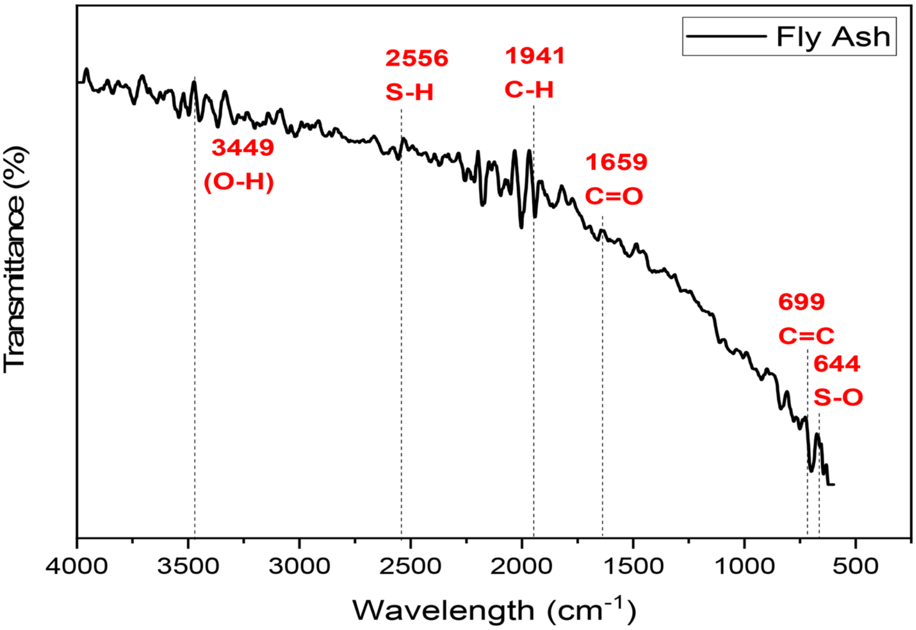

Fig. 3 FTIR of the fly ash sample.

In addition, BET analysis revealed that fuel fly ash has macro- and micro-pores and the BET surface area of fly ash is 17.9 $m^2\ g^{-1}$. The total pore volume of fly ash is 1.238 cc g^{-1} with a sufficient percentage of macro- and micro-pores. During catalytic pyrolysis of LDPE random bond breaking took place in macro-pores, producing short chain radicals. Thereafter, these short chain radicals entered into microspores for further bond breaking and rearrangement of molecules took place to form a new product.

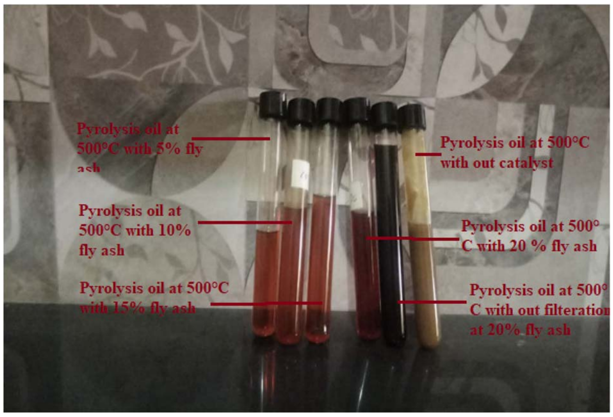

Fig. 5 Pyrolysis oil samples collected from different experiments.

3.3 Non-catalytic pyrolysis of plastic waste

Thermal pyrolysis of waste LDPE bags was carried out at temperatures ranging from 450 °C to 600 °C. At 500 °C, the liquid yield was observed to be highest compared to that at 450 °C as shown in Fig. 4. This is likely due to the fact that high temperatures enhanced the bond breaking resulting in enhanced production of volatiles from LDPE and oil yield. However, the liquid yield decreased while the gaseous yield increased during pyrolysis at temperature higher than 500 °C which is associated with secondary reactions that cracked vapors. The quantity and quality of the products were both affected by temperature, with long chain compounds being produced at low temperatures and short chain compounds being produced at high temperatures due to cracking of C–C bonds.[45] Additionally, some researchers have reported that aromatic compounds were produced at high temperatures due to secondary reactions.[46]

In this study, the maximum liquid yield of 72% was obtained at 500 °C, while the maximum gas yield of 39% was obtained at 600 °C. The liquid yield was observed to decrease at 550 °C while the gas yield increased. It can be observed in Fig. 4 that the maximum liquid yield was obtained at 500 °C and the minimum at 450 °C while the maximum conversion was observed at 600 °C (Fig. 5).

It implies that the cracking reaction is increased by increasing the pyrolysis reaction temperature.[47] The cracking reaction breaks the bonds of hydrocarbons, and this process is endothermic requiring a large amount of heat energy to break the bonds.[48] The increase in temperature leads to an increase in the cracking reaction and the production of gas.[49] At high temperatures, C–C bonds break, resulting in an increase in

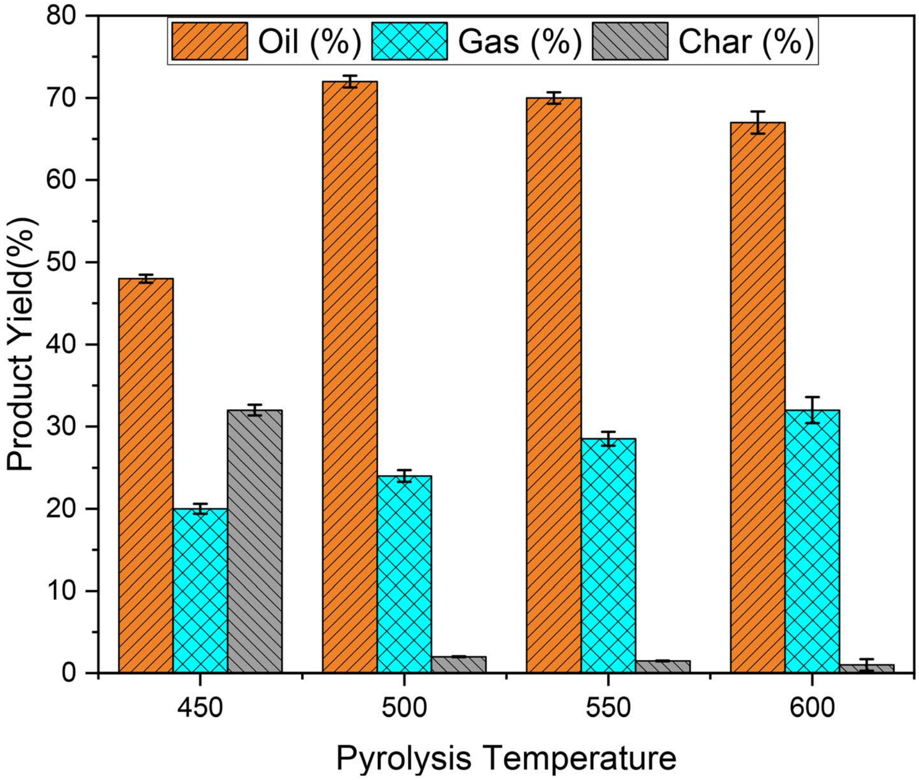

Fig. 4 Pyrolysis of LDPE at various temperatures (°C).

Table 3 Percentage composition of the aromatized product at different temperatures

Compounds	500 °C	550 °C	600 °C
Ethyl benzene	2.53	2.60	3.65
Benzene propyl	0.70	0.80	0.83
Indene and derivatives	1.29	1.7	5.87
Naphthalene and derivatives	0.10	0.29	1.34

aromatic contents such as ethyl benzene, benzene propyl, and indene, and its derivatives. The GC/MS results showed an increase in the concentration of ethyl benzene from 2.53% to 3.65%, benzene propyl from 0.70% to 0.83%, and indene and its derivatives from 1.29% to 5.87% with the increase in temperature as given in Table 3.

The heating value of liquid oil decreased as the temperature of the reaction increased. This is attributed to enhanced secondary reactions that occur and break the vapors into the gas at higher temperatures, which reduces the heating value of the remaining liquid. Furthermore, the heating value range observed in this study was between 21 243 and 23 800 Btu lb^{-1}, which is higher than the heating value of diesel fuel (18 200 Btu lb^{-1}) and also higher than the heating value of pyro-oil reported by Khairil *et al.*[50] This study also found that increasing the temperature led to an increase in aromatization and a decrease in the hydrogen carbon ratio, which further reduced the GCV of the oil as shown in Fig. 6.

Furthermore, the presence of water in fuel can affect both its heating value and flash point. When fuel is exposed to high temperatures during pyrolysis, the resulting oil yield will contain less water and therefore ignite more easily with a lower flash point.[51] In this specific study, the flash point of the liquid produced was found to be within the range of 32.5 °C to 40 °C, which is similar to the flash point of kerosene (38–72 °C) but lower than that of diesel fuel. The data in Fig. 7 also indicate that as temperature increases, the flash point of the liquid decreases.

Based on the GC/TCD results, it is evident that the reaction produced CH_4 and H_2 gases. The lowest gas yield was produced at 450 °C and highest at 600 °C as shown in Fig. 8. As the pyrolysis temperature increased, the gaseous products also increased because the C–C bonds are cracked at higher temperatures.[45] The results indicate that both CH_4 and H_2 gases increased as the temperature increased especially at 600 °C. The production of aromatic and light hydrocarbons was also observed to increase with temperature through various reactions which could also increase the gas formation with the increase in temperature.[52] The GC/TCD results further show that methane gas production increased continuously with increasing temperature, reaching up to 35%. The hydrogen yield was also observed to increase with temperature, with a maximum yield of 5.0%. The increase in gaseous products is attributed to the breaking of bonds at high temperatures as depicted in Fig. 8.

3.4 Catalytic pyrolysis of plastic waste

Gaseous products were produced during both thermal and catalytic pyrolysis; however, the percentage of gaseous products was higher in the latter. Specifically, at a temperature of 500 °C, the gas yield was 24% in thermal pyrolysis, while in catalytic pyrolysis, the maximum gas yield was 35.5%. Furthermore, at a higher catalyst to reactant ratio the yield of gaseous fractions

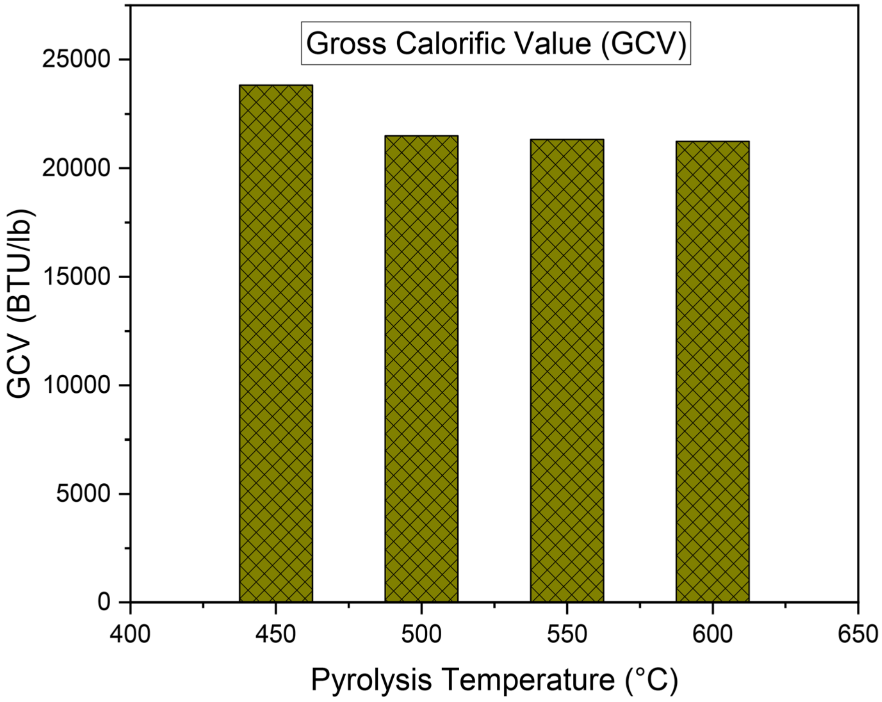

Fig. 6 GCV of pyrolysis oil without the fly ash catalyst.

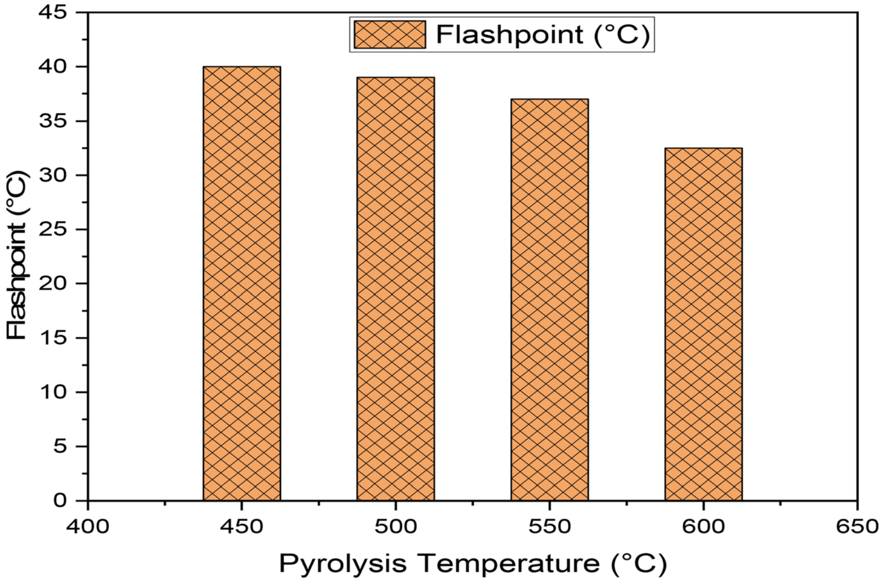

Fig. 7 The flash point of liquid oil at different pyrolysis temperatures.

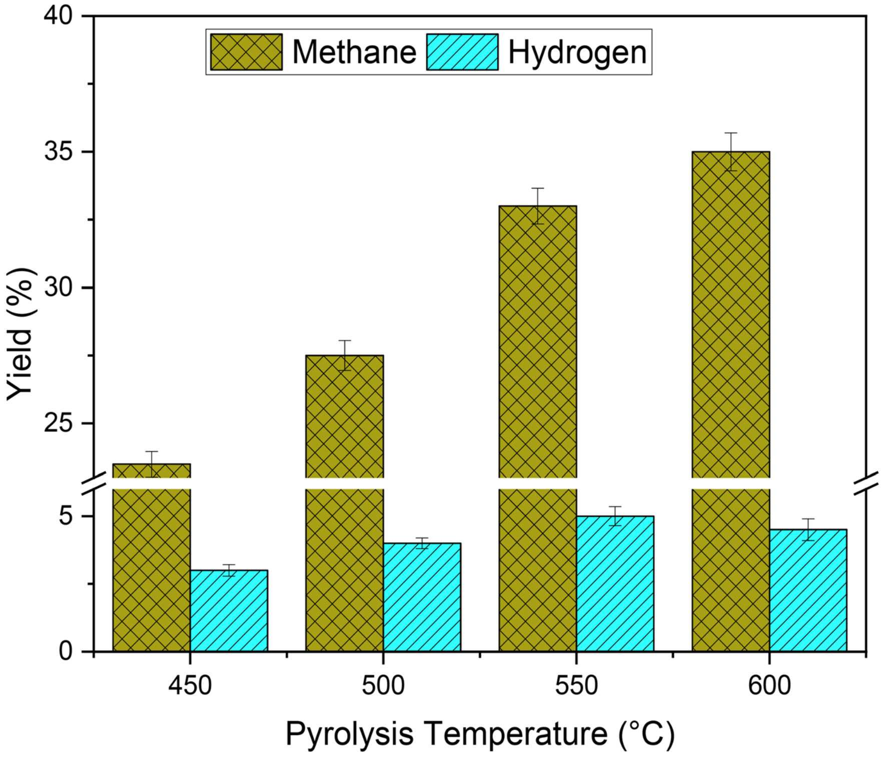

Fig. 8 Gaseous product yields at different pyrolysis temperatures.

showed an increasing trend.[53,54] Table 4 likely shows the yield of gas at different percentages of the fly ash catalyst. This indicated that the catalyst had the ability to break the C–C and C–H bonds present in the hydrocarbons, which resulted in increased C–C bond breaking reactions at higher temperatures or with increased catalytic sites. When the catalyst loading was increased to 20%, the bond dissociation was enhanced resulting in a larger quantity of gas being produced such as methane and hydrogen. It was also observed that their production increased as the percentage of catalyst was increased, as the catalyst increases the number of C–C bonds broken and can lead to the secondary reaction of vapors thereby increasing the gas yield. This process results in the production of hydrogen-rich gases and methane, as indicated in Table 5.

Table 4 % yield of gaseous products at different loadings of fly ash catalysts

Samples with catalyst	Temperature (°C)	Gases (%)
P-500-FA-5	500	28
P-500-FA-10	500	30.5
P-500-FA-15	500	33.5
P-500-FA-20	500	35.5

Table 5 Percentage composition of gaseous products

Catalyst (fly ash%)	Temperature (°C)	CH_4 (%)	Hydrogen (%)	Others (%)
P-500-FA-5	500	32.5	2.3	63.2
P-500-FA-10	500	37.5	3.2	59.3
P-500-FA-15	500	38.5	3.4	58.6
P-500-FA-20	500	44	3.8	52.2

Table 6 Elemental composition of residue char after pyrolysis

	Percentages (%)	
Element	Residue-1	Residue-2
Carbon	68.69	82.78
Hydrogen	4.23	5.68
Nitrogen	1.52	1.68
Sulphur	0.0	0.0

By increasing the percentage of catalyst, the catalytic reforming reaction is increased, which leads to an increase in the production of hydrogen and methane gases. The macro- and micro-pores of fly ash provide maximum reaction times and active sites such as C–O, C=C, and OH, which increase the rate of the reaction. As a result, there is a rise in alkane and kerosene production with smaller hydrocarbon chains and greater gas yield.

The pyrolysis process produced a solid residue, or char, which was collected after cooling the reactor. The amount of char produced was highest at 450 °C and lowest at 600 °C, indicating an inverse relationship between char production and temperature. The elemental analysis of the char showed that it contained a high percentage of carbon (82.78%) and a moderate amount of hydrogen (5.68%). These results suggest that the char could potentially be used as a fuel in furnaces or boilers. Furthermore, char has been found to have a high GCV ranging from 18.84 MJ kg^{-1} to 36.49 MJ kg^{-1}.[27] This means that it has the potential to be used as a source of energy. Additionally, the presence of hydrogen in the char could be beneficial in pyrolysis reactions, as hydrogenation reactions can occur during the process. This could potentially increase the yield of desired products and improve the efficiency of the process. Overall, the results suggest that the char residue produced during pyrolysis has potential as a fuel source and could be useful in pyrolysis processes. Further testing and analysis would be necessary to fully understand the properties and potential applications of this material. Liquid oil can be used as fuel in engines and boilers, while the solid residue can be used as an adsorbent in wastewater treatment applications. Overall, the use of char and other products can provide a sustainable and environmentally friendly source of energy and industrial materials while also reducing waste and greenhouse gas emissions (Table 6).[55]

The gross calorific value (GCV) of a fuel is an important indicator of its energy efficiency. The gross calorific value of pyrolysis oil of waste plastic in the presence of fuel fly ash as a catalyst is given in Fig. 9. The GCV of the liquid product obtained by pyrolysis of waste plastic with fuel oil fly ash is in the range of 21 620–21 920 Btu lb^{-1}, and these values are higher than the GCV of liquid obtained from thermal pyrolysis of waste plastic without the fly ash catalyst. Furthermore, the GCV values obtained from the pyrolysis of waste plastic with the fuel fly ash catalyst are significantly high and are very close to the GCV of conventional diesel fuel.[56,57] Therefore, it is possible to use this pyrolysis oil as a transportation fuel by blending it with conventional diesel fuel. It is important to note that additional testing and evaluation may be necessary to determine the feasibility and practicality of using pyrolysis oil from waste plastic as a transportation fuel and such evaluation and testing were reported by Khairil *et al.*[50] However, the high GCV values suggest that this fuel source could have the potential for reducing reliance on traditional fossil fuels and promoting sustainability.

The flash point is indeed an important property of any fuel as it is a measure of its safety during transportation, storage and handling, and use. The flash point of pyrolysis oil obtained from catalytic pyrolysis of waste plastic with different ratios of fuel fly ash is shown in Fig. 10. It can be observed that the flash point of pyrolysis oil is lower than that of conventional diesel. This means that transportation of such fuel requires special precautions such as using proper containers, avoiding ignition sources, and complying with safety regulations. One way to use pyrolysis oil as a transportation fuel is by blending it with conventional diesel or kerosene. By blending, the flash point of the resulting fuel can be increased to a level that meets safety requirements for transportation. The appropriate blend ratio depends on the flash point of the pyrolysis oil and the flash point requirement for transportation. Moreover, the flash point of the pyrolysis oil can be improved through fractional distillation. This process separates the oil into different fractions based on their boiling points, with lighter fractions such as gasoline and kerosene being separated first followed by heavier fractions such as diesel and residual oil. By selectively removing the lighter fractions, the flash point of the remaining oil can be increased making it safer to handle and transport.

In this study, the viscosity of plastic oil was measured at 40 °C, and it was found to be 1.28 cP with a 20% fly ash catalyst and 1.29 cP with a 15% fly ash catalyst. It is important to note that higher viscosity fuels consume more fuel and increase friction in engines which can reduce their efficiency. This can also affect the combustion process in boilers and requires additional energy to raise the temperature of the fuel for complete combustion. However, this study found that waste plastic

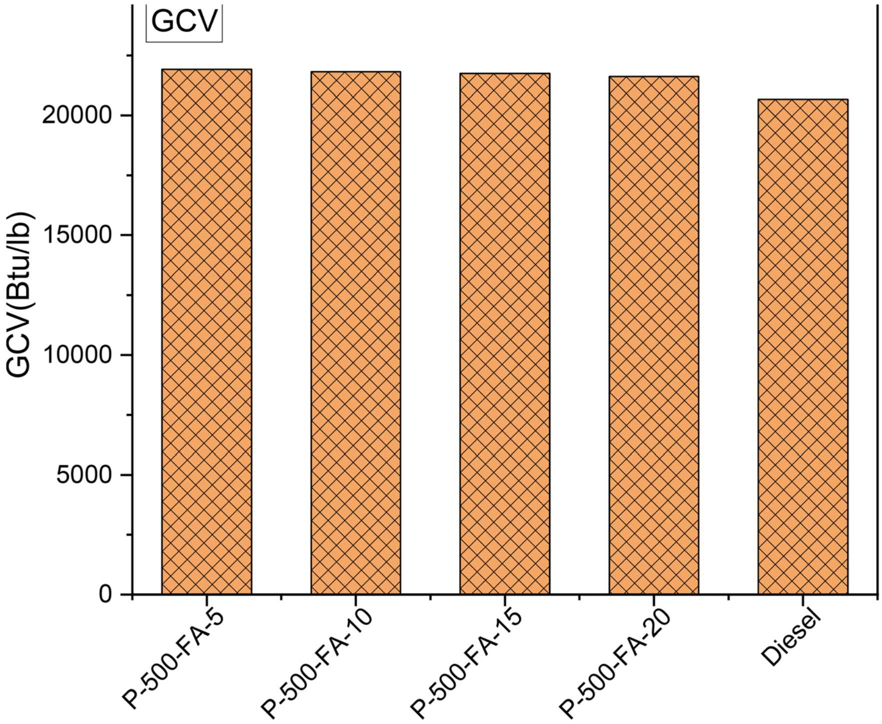

Fig. 9 GCV of pyrolysis oil with the fly ash catalyst with different percentages.

pyrolysis oil obtained at 500 °C pyrolysis temperature with fuel ash as a catalyst had a comparatively lower viscosity of 1.28 cP, which is lower than that of kerosene and diesel as shown in Fig. 11. Kerosene oil has a viscosity of 1.5 cP while those of diesel and light diesel fuel are 4.162 cP and 9.0 cP respectively. Therefore, this fuel could be a suitable alternative for

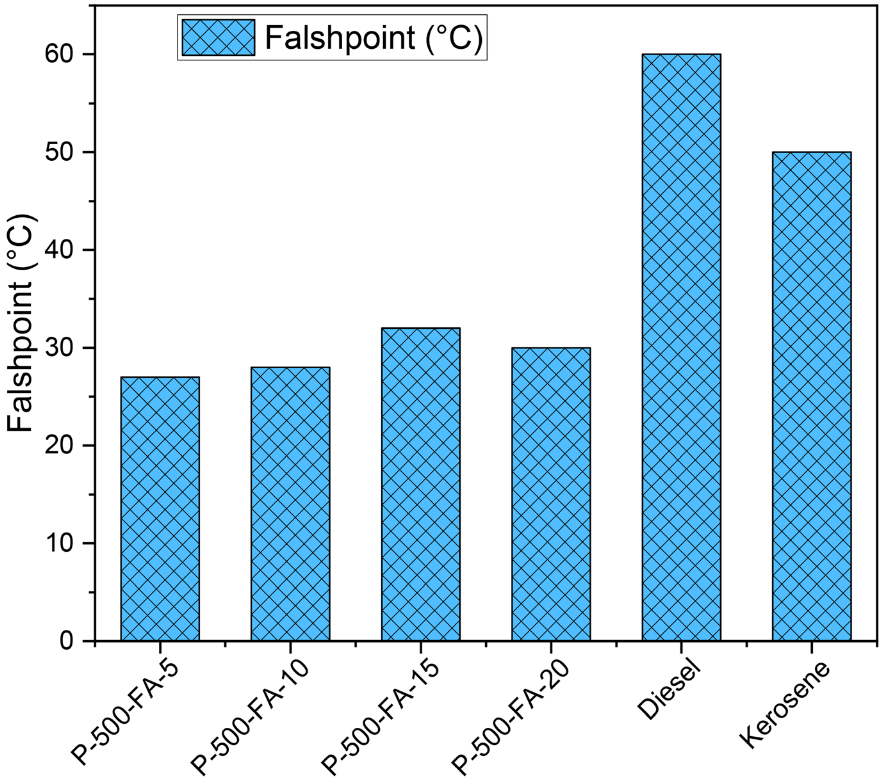

Fig. 10 The flash point of waste plastic oil and conventional fuels.

transportation or stove use by blending with conventional kerosene and diesel.[58]

The use of catalysts in pyrolysis processes can be beneficial in improving the quality of the products produced, including the heating value of the oil. However, the effectiveness of a particular catalyst will depend on a variety of factors, including the type of feedstock being used and the specific conditions of the pyrolysis process. This study found that the use of a fly ash catalyst increased the yield and quality of pyrolysis products. Specifically, the maximum yield of liquid oil was 70% with a 5% fly ash catalyst and 66% with a 20% catalyst. The gas yield was highest with the 20% catalyst and lowest with the 5% catalyst. The gross calorific value (GCV) of the oil was also increased up to 21 920 Btu lb^{-1} with the use of the catalyst, which is higher than the GCV of liquid produced in thermal pyrolysis without the catalyst and greater than conventional diesel which is up to 20 670 Btu lb^{-1}.[59]

Furthermore, to know the effect of a fly ash catalyst on the yield and composition of liquid oil produced from thermal pyrolysis of fuel at different percentages of the catalyst, experiments were conducted at a fixed temperature of 500 °C, which was found to be the optimum temperature for catalytic pyrolysis. We compared the results with those obtained from thermal pyrolysis without a catalyst, which produced the maximum oil yield. The results of the experiments showed that the use of a fly ash catalyst led to an increase in the alkane content of the liquid oil, with the alkane percentage reaching 39.75%. Additionally, the kerosene and diesel fractions of the liquid oil were found to increase with an increase in the percentage of the fly ash catalyst, while the heavy fractions decreased. This can be attributed to the presence of iron (Fe_2O_3) in the composition of the fly ash catalyst, which likely promoted the formation of lighter hydrocarbon fractions through catalytic cracking and hydrogenation reactions. S. Malik and H. Gulab reported similar results in pyrolysis of waste plastic by using iron as the catalyst.[60]

The addition of the fly ash catalyst increased the yield of kerosene fractions (C7 to C16) in the oil fraction obtained from catalytic pyrolysis using fly ash as a catalyst which can be used as jet fuel after upgradation.[18] As the amount of fly ash catalyst used in the process increases (from 5% to 20%), the percentage of kerosene fractions in the oil products also increases (from 53.23% to 67.86%). This indicates that the fly ash catalyst has a positive effect on the production of kerosene fractions. Kerosene fractions can be separated from other compounds using fractional distillation and can be further upgraded for utilization as jet fuel. Additionally, compounds in the C17 to C22 range can be used as diesel fuel for heavy vehicles.[61] Some researchers used a HZSM-5 catalyst at 400 °C to conduct pyrolysis of waste plastic. The use of this catalyst resulted in the strong cracking of the plastic, leading to an increase in light hydrocarbon fractions such as kerosene oil yield and a decrease in viscous fractions. Furthermore, the addition of raw fly-ash plastic as a catalyst led to significant improvements in the composition of alkanes, as seen in GCMS studies. This improvement was attributed to the presence of MgO and C in the fly ash.[62,63] The hydrogen production demonstrated an increase with the rise in the percentage of fly ash catalyst,

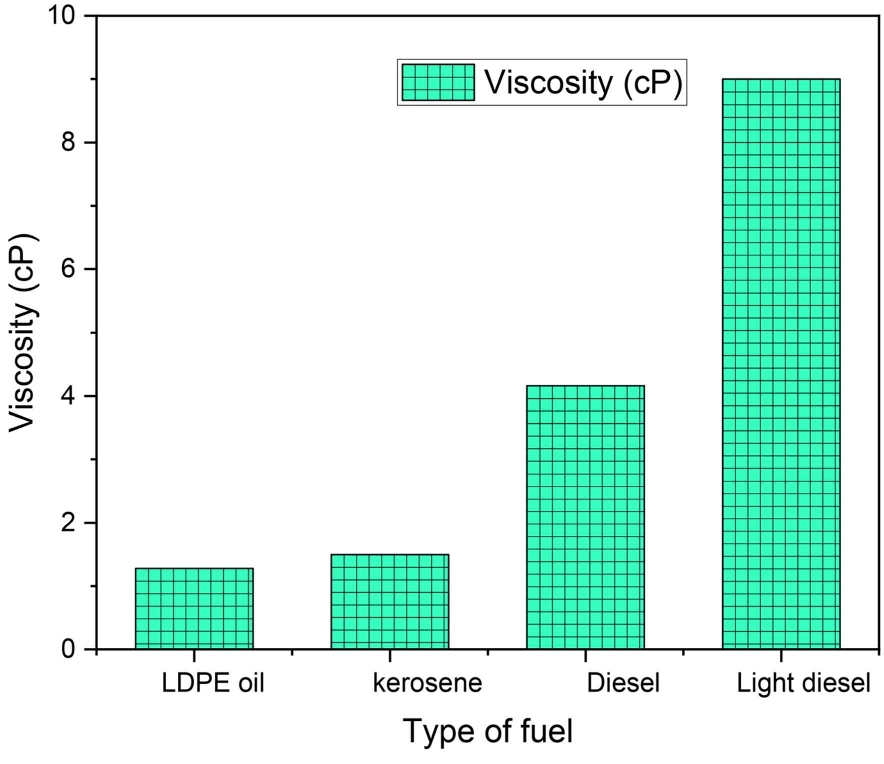

Fig. 11 Comparison of the viscosity of different fuels with waste plastic pyrolysis oil at 40 °C.

attributed to the presence of MgO in the fly ash. Similar findings were reported by Huo *et al.*, who observed that activated carbon modified with MgO could enhance selectivity towards alkylated phenols during the catalytic pyrolysis of biomass, leading to increased hydrogen production in the catalytic pyrolysis of LDPE due to the presence of MgO in the fly ash catalyst.[64]

It was observed that the addition of a fly ash catalyst during pyrolysis results in an oil product with a higher gross calorific value (GCV) compared to thermal pyrolysis without the catalyst at the same temperature. Specifically, the GCV of oil produced with a 5% fly ash catalyst was 21 919 Btu lb^{-1}, while the GCV of oil produced without the catalyst at 500 °C was 21 496 Btu lb^{-1} (according to Fig. 8). Additionally, the liquid oil produced with a 20% fly ash catalyst had a composition of 90% aliphatic and 10% aromatic compounds. The flash point of the liquid oil was also lower than that of the oil produced without the fly ash catalyst at 500 °C, with a minimum of 27 °C and a maximum of 32 °C. Based on these results, it was suggested that the pyrolysis oil could be used as a transportation fuel by blending it with conventional diesel. Some researchers recommended a blending ratio of 20 to 80% for optimal engine performance.[58,65]

3.5 Chemical composition of pyrolysis oil

3.5.1 FTIR of pyrolysis oil. The FTIR spectrograms of pyrolysis oil with 5% fly ash as a catalyst are shown in Fig. 12. The FTIR spectrum indicates the presence of several functional groups in the sample. The peaks at 2920 cm^{-1} and 2854.78 cm^{-1} correspond to CH_3, CH_2, and CH groups, indicating the presence of alkanes in the sample. Another peak observed at 1456.59 cm^{-1} also corresponds to CH_3 and CH_2 groups, suggesting the presence of alkanes. The peak at 1378 cm^{-1} represents O–H groups, indicating the presence of alcohols or phenols in the sample. Furthermore, the peak at 1513 cm^{-1} corresponds to NH groups, indicating the presence of secondary amines in the sample. Finally, the peak at 1642 cm^{-1} corresponds to NH_2, $=CH$, and $=CH_2$ groups, indicating the presence of amines and alkenes in the sample. These results provide valuable information about the chemical composition of the pyrolysis oil and suggest that it contains a mixture of alkanes, alcohols or phenols, secondary amines, and amines or alkenes.[66]

Furthermore, Fig. 12 shows the results of FTIR analysis of pyrolysis oil obtained at 500 °C temperature with a 20% fly ash catalyst. The peaks observed at 2922 cm^{-1}, 2856 cm^{-1}, and 1456 cm^{-1} suggest the presence of alkanes, as they correspond to the C–H stretching of alkanes. Additionally, peaks at 1642.83 cm^{-1}, 991.2 cm^{-1}, and 777 cm^{-1} indicate the presence of alkenes and aromatics. Specifically, the peak at 1642.83 cm^{-1} corresponds to C–H bending of alkenes, while the peak at 777 cm^{-1} corresponds to C–H bending of aromatics. The peak at 991.2 cm^{-1} corresponds to O–H bending of phenol, which suggests the presence of phenolic compounds in the pyrolysis oil sample. Finally, the peak at 3420 cm^{-1} corresponds to the C=C bending of alkenes. Overall, the results of the FTIR analysis suggest that the pyrolysis oil sample contains a mixture of alkanes, alkenes, and aromatics, with the presence of phenolic compounds. The use of fly ash as a catalyst may have influenced the chemical composition of the pyrolysis oil, which could have important implications for its potential applications (Table 7).[37]

3.5.2 GCMS of pyrolysis oil. Furthermore, ESI Tables S1–S4† illustrate the overall GCMS result of samples with 5, 10, 15 and 20% fly ash at 500 °C which are present in the ESI file.† Fig. 13 shows the comparison of carbon fractions of all these samples with different percentages of fly ash catalyst.

Oil samples contain a variety of hydrocarbons with carbon chain lengths ranging from C7 to C27 which are reported in Tables S1–S4.† The major components include heptane, benzene, cyclohexane, 1-methyl octene, octane, nonane, nonene, undecane, dodecane, tridecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane, icosane, tricosane, tetracosane, heptacosane, and docosane, which are tabulated in Tables S1–S4.†

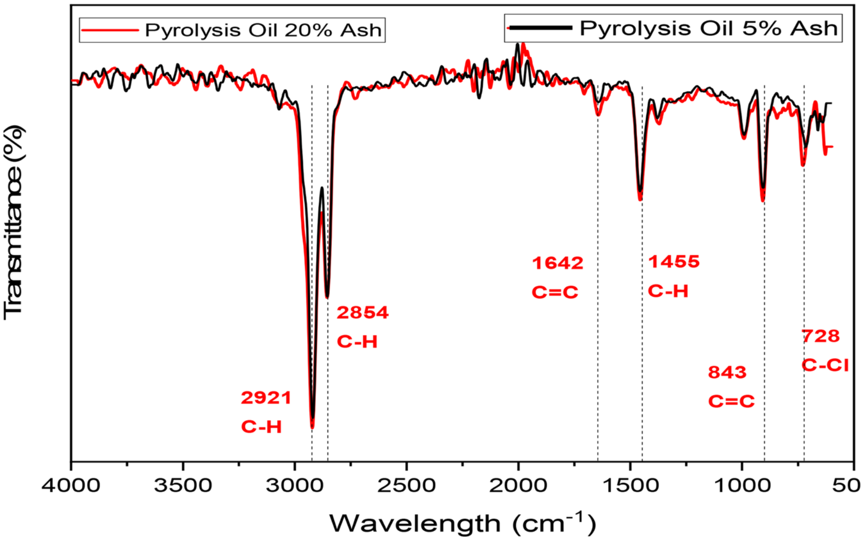

Fig. 12 FTIR analysis of pyrolysis oil with 5% and 20% fly ash as catalysts at 500 °C.

Table 7 Yield of waste plastic catalytic pyrolysis products

Sample code	Temperature (°C)	Oil (%)	Gas (%)	Char (%)
P-500-FA-5	500	70	28	2
P-500-FA-10	500	69	29.5	1.5
P-500-FA-15	500	68	31.5	0.5
P-500-FA-20	500	66	33.5	0.5

Based on the GCMS results and literature, it appears that the thermal degradation of waste plastic proceeds through a random scission reaction, primarily due to a large number of hydrocarbons present.[67] The presence of carbon double bonds in the plastic also contributes to the formation of alkene compounds, which are more stable than single bonds.[68]

Fly ash is used as a catalyst in the degradation process due to its acidic nature, porosity and inherent metal oxides which help to break down plastic waste.[18,32,69] By increasing the percentage of catalyst used from 5% to 20%, the area % of light hydrocarbons in the resulting mixture (in the range of C7–C16) was increased from 53% to 68%, while the area % of heavy hydrocarbons was decreased from 18% to 4% as shown in Fig. 13, and the same results were reported in other study.[70] Furthermore, the fly ash catalyst for the pyrolysis process resulted in an increase in alkane percentages as given in Fig. 14 with the highest percentage of alkanes (39.75%) observed with the 20% catalyst while the lowest percentage of alkanes (16%) was found in thermal pyrolysis at 500 °C without the fly ash catalyst.[63] The addition of the fly ash catalyst resulted in a decrease in heavy fractions, and an increase in light alkanes, which suggests that the catalyst has the potential to break down heavy fractions. The presence of MgO in the fly ash catalyst may also contribute to changes in the quality of plastic oil leading to an increase in alkane percentages and hydrogen production.[64] Aromatic hydrocarbons such as benzene, toluene, and ethylbenzene are commonly found in crude oil and other petroleum products. These compounds have a ring-like structure and are characterized by their distinct odor and high reactivity. Compounds have low boiling points and are often separated from the heavier fractions during refining processes. Fly ash catalysts can be used to break down heavy hydrocarbon fractions into smaller, more useful compounds.[42] The acidic nature of fly ash can help to cleave the larger hydrocarbon molecules, leading to an increase in the concentration of aromatic and light hydrocarbon fractions.[22] In the study by Saptoadi *et al.*, the researchers investigated the feasibility of using pyrolysis oil as a fuel in a kerosene stove. They mixed the pyrolysis oil with conventional kerosene oil at various ratios and tested the combustion efficiency and emissions of the mixed fuels.[71]

3.5.3 NMR of pyrolysis oil.

The proton nuclear magnetic resonance (HNMR) spectrum of aromatic and aliphatic hydrocarbons is presented in ESI Fig. S2.† The HNMR spectrum shows a range of chemical shifts in the region of 0.7–7.365 ppm. In this range, there are different types of hydrogen atoms that can be observed. The aliphatic hydrogen atoms, which are attached to carbon atoms except for carbon–carbon double bonds, are observed in the region from 0.7 to 1.5 ppm. The aliphatic hydrogen atoms that are attached to carbon–carbon

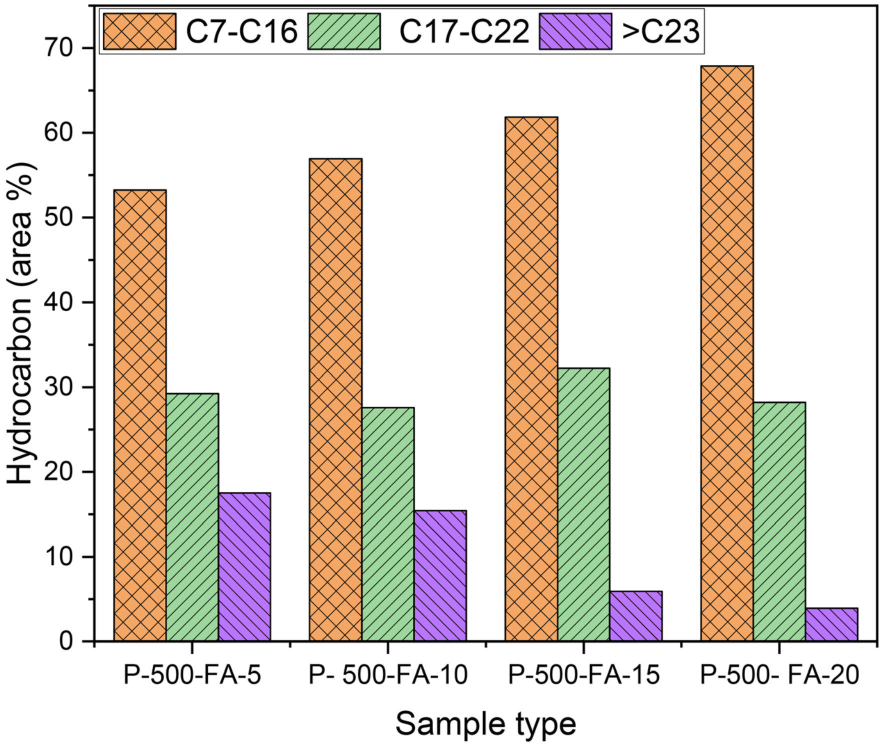

Fig. 13 Comparison of GC/MS results of samples.

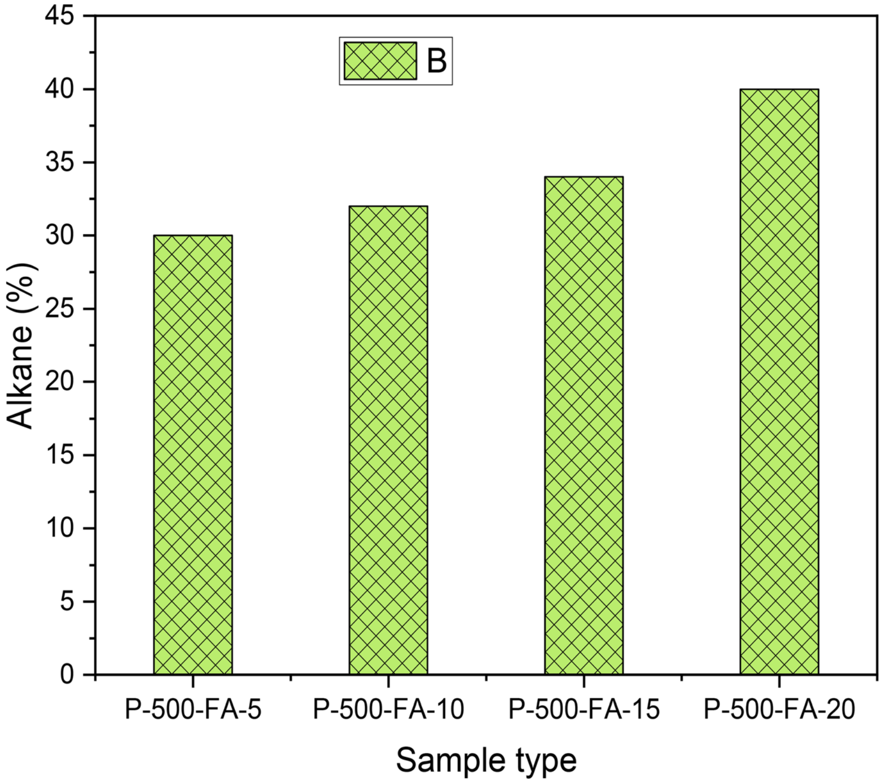

Fig. 14 Comparison of alkane production in pyrolysis oil under different catalyst loading conditions.

double bonds are observed in the region from 1.5 to 3.0 ppm. The $CH_3\alpha$ group is observed in a concentration range of 2–2.4 ppm, while the $CH_3\beta$ group is observed in the concentration range of 2–2.4 ppm. The CH_3y groups are found in the concentration range of 0.5–0.95 ppm. The alkane groups of CH/CH_2 are observed in the concentration range of 1.0–2.0 ppm. The olefinic hydrocarbons are observed in the region from 4.0 to 4.5 ppm. The aromatic hydrogen atoms and aromatic hydrocarbons are observed over 4.5 ppm. It is interesting to note that 86.30% of the hydrocarbons in the compound are aliphatic, while the remaining 13.70% are aromatic.

The NMR spectra of the liquid product of pyrolysis of waste polythene are shown in Fig. S3.† The CNMR spectra showed the presence of different hydrocarbon groups in the liquid oil such as α-methyl (CH_3–) at 14.40–23 ppm, methyl (CH_3–) at 13–14.40 ppm, methylene (–CH_2–) at 23–34 ppm, and methine (=CH–) at 34–41 ppm. The chemical shifts at 13–23 ppm and 23–34 ppm were attributed to the aliphatic alkyl (CH_3) and aliphatic alkene (CH_2) groups, respectively. The presence of both aromatic and aliphatic linkages within the liquid oil structure was observed at a chemical shift of 34–41 ppm, which could be due to bridging of aliphatic to aromatic groups. The shift range of 113–129.5 and 129–139.26 indicated C–H bond shifting. Based on the CNMR spectra, it was found that the percentage of aliphatic and aromatic compounds in the liquid oil was 87% and 13%, respectively. These findings provide important insights into the chemical composition of the liquid product obtained from the pyrolysis of waste polyethylene, which could be useful for further characterization and optimization of the pyrolysis process.[72] Based on these observations, it can be concluded that the liquid product of pyrolysis of waste polyethylene contains both aliphatic and aromatic hydrocarbons. The majority of the hydrocarbons are aliphatic, while only a small portion of them is aromatic. The CNMR spectra also indicate the presence of different types of chemical bonds, including aliphatic alkyl, aliphatic alkene, and bridging of aliphatic to aromatic. Nepu Saha *et al.* conducted a similar study, pyrolyzing mixed plastic without a catalyst, and utilized the ^1H NMR technique to analyze the pyro-oil. Their findings revealed that the pyro-oil consisted of approximately 60% aliphatic compounds and 40% aromatic compounds[73] but in the present study fly ash was used as a catalyst which generated more aliphatic compounds than aromatics. In other study, Khan *et al.* employed hydrogen in the copyrolysis of waste tires and Thar coal blends. Their analysis using ^{13}C NMR indicated the presence of 35% aliphatic and 65% aromatic compounds, while ^1H NMR[74] revealed 45% aliphatic and 55% aromatic compounds. In the study conducted by Sana *et al.*, they performed copyrolysis of Thar coal, waste plastic, and waste oil in the presence of hydrogen. Their analysis using the ^{13}C NMR technique revealed the presence of 84% aliphatic and 16% aromatic compounds.[75]

Furthermore, a comparison of the main products obtained between the current and previous studies was conducted, and the details are listed in Table 8. The previous studies used different catalysts to enhance the production of gaseous and

Table 8 Comparison of different parameters of waste plastic pyrolysis oil with the literature

Raw material	Temperature (°C)	Catalyst	Gaseous products	Liquid products	References
LDPE	500	Activated carbon	H_2, C_1–C_4 hydrocarbons, 28 wt%	C_8–C_{16} (paraffins: 82.9 area%, aromatics: 14.6 area%), 72 wt%	76
Plastic	400	HZSM	CO_2, H_2, CH_4, C_2H_4, C_2H_6, 3 wt%	C_7–C_{21}, 78 wt%	61
Polystyrene	410	MCM-41	Gases 10.94 wt%	Liquid yield, 62.18 wt%	77
HDPE	375	ZSM-5	H_2, CH_4 gases 28 wt%	15% aromatics, 31% alkanes, 53% cycloalkanes, 67 wt%	78
LDPE	500	Fly ash 20 wt%	H_2 and CH_4, 33.5 wt%	C7–C16 68 wt%, C17–C22 28 wt%, C23 and above 4 wt%, liquid yield 64 wt%, 40% alkane	This work
LDPE	500	Fly ash 10 wt%	H_2 and CH_4, 29 wt%	C7–C16 57 wt%, C17–C22 28 wt%, C23 and above 15 wt%, yield. 69 wt%, 34% alkane	This work

liquid products to obtain useful jet-fuels and petroleum-like hydrocarbons with a HZSM catalyst.[21] The catalysts used in these previous studies have acidic properties, which promote the production of C7–C27 aromatics, olefins, and alkanes. The use of the fly ash catalyst appears to be particularly effective in this regard.

3.5.4 Reaction mechanism.

Fig. 15 illustrates the mechanistic aspects of pyro-oil formation during the process. A significant reaction that occurs during pyrolysis is thermal shock, leading to the breakdown of various bonds in LDPE. The utilization of thermal and catalytic processes has resulted in a notable alteration in the degradation pattern. Fig. 15a illustrates the impact of thermal fragmentation on the pyrolysis products. The prevailing products were primarily cyclic in nature, including cyclohexanes, benzene ring-structured compounds, decenes, and aliphatic compounds with a carbon chain length greater than 20 (C > 20). Meanwhile there were some lower hydrocarbons with a carbon chain length of less than 10 (C < 10) and gases like CH_4 and H_2, and their abundance was not particularly significant. Thermal shock caused the decomposition of LDPE into cyclic or aliphatic fragments, although the evidence for second and third stage fragmentation was not highly apparent. Fig. 15b illustrates the impact of the catalyst on the fragmentation by-products of LDPE. The GC-MS results demonstrate the presence of all frames of fragments. The catalyst has initiated a mechanism that transformed the fragmented products into smaller molecular weight fractions. The initial thermal shocks resulted in the formation of free radical products, which included breakdown of chains and similar processes, which were observed in previous studies. These fragmented components either stabilized or isomerized and cyclized, leading to the formation of various smaller fragments.[79–81] On the catalyst surface, free radicals were found to be stabilized through Brønsted and Lewis acid sites, with the fly ash in this study being acidic due to its low pH value. These compounds underwent further cycling through thermal shocks, breaking down into fragments, and were subsequently stabilized again into smaller fractions on the catalyst's active sites. It is due to these stabilization and initiation reactions that the abundance of lower hydrocarbons was higher in the case of the fly ash catalyst compared to thermal fragmentation. Through the processes of isomerization and cyclization, naphthenic hydrocarbons can be formed from the resulting olefins. Subsequently, the metal oxides present in the fly ash catalyst can convert these naphthenic hydrocarbons into lower hydrocarbons and hydrogen. The dehydrogenation process plays a crucial role in petroleum refining, and metal oxides are key catalysts in the catalytic reforming process to produce H_2.[44,64] Subsequently, the metal oxides, particularly Fe_2O_3 and MgO in the fly ash catalyst, facilitate the conversion of naphthenic hydrocarbons into lower hydrocarbons and hydrogen. The dehydrogenation process plays a pivotal role in producing H_2 in petroleum refineries, with metal oxides performing a key function in the catalytic reforming process.[44,59,63] Fe_2O_3 enhances the hydrogenation activity of fly ash, leading to a decrease in aromatic yield and an increase in aliphatic compounds during the process.[82] The incorporation of fly ash in waste plastic altered the selectivity of products. As previously explained, an increase in the fly ash ratio resulted in higher production of lighter hydrocarbons and a decrease in heavy hydrocarbons. During plastic pyrolysis, coke is generated and deposits on the catalyst, thereby diminishing the catalyst's efficiency. This occurrence contributes to an increase in the overall production cost and a decrease in production efficiency. However, in this study, fuel oil fly ash was utilized as a catalyst, which proves to be more cost-effective compared to other catalysts. Moreover, fuel oil fly ash's acidic nature helps to prevent the deposition of coke during the process.[83] Secondly, pyro-oil and pyro gas can serve as alternative fuels, potentially conserving fossil fuel resources for the future.[84] The overall efficiency of the system can be improved by employing fly ash as a catalyst, while also contributing to the mitigation of hazardous waste in the environment. This approach offers a superior waste management option compared to gasification and non-catalytic processes because gasification temperature is higher than pyrolysis temperature. More energy is required for gasification, and furthermore the Fischer Tropsch process is necessary to generate liquid oil.[85] Catalytic pyrolysis is also more efficient than noncatalytic pyrolysis of plastic because liquid oil produced in noncatalytic pyrolysis is mostly in the wax form at

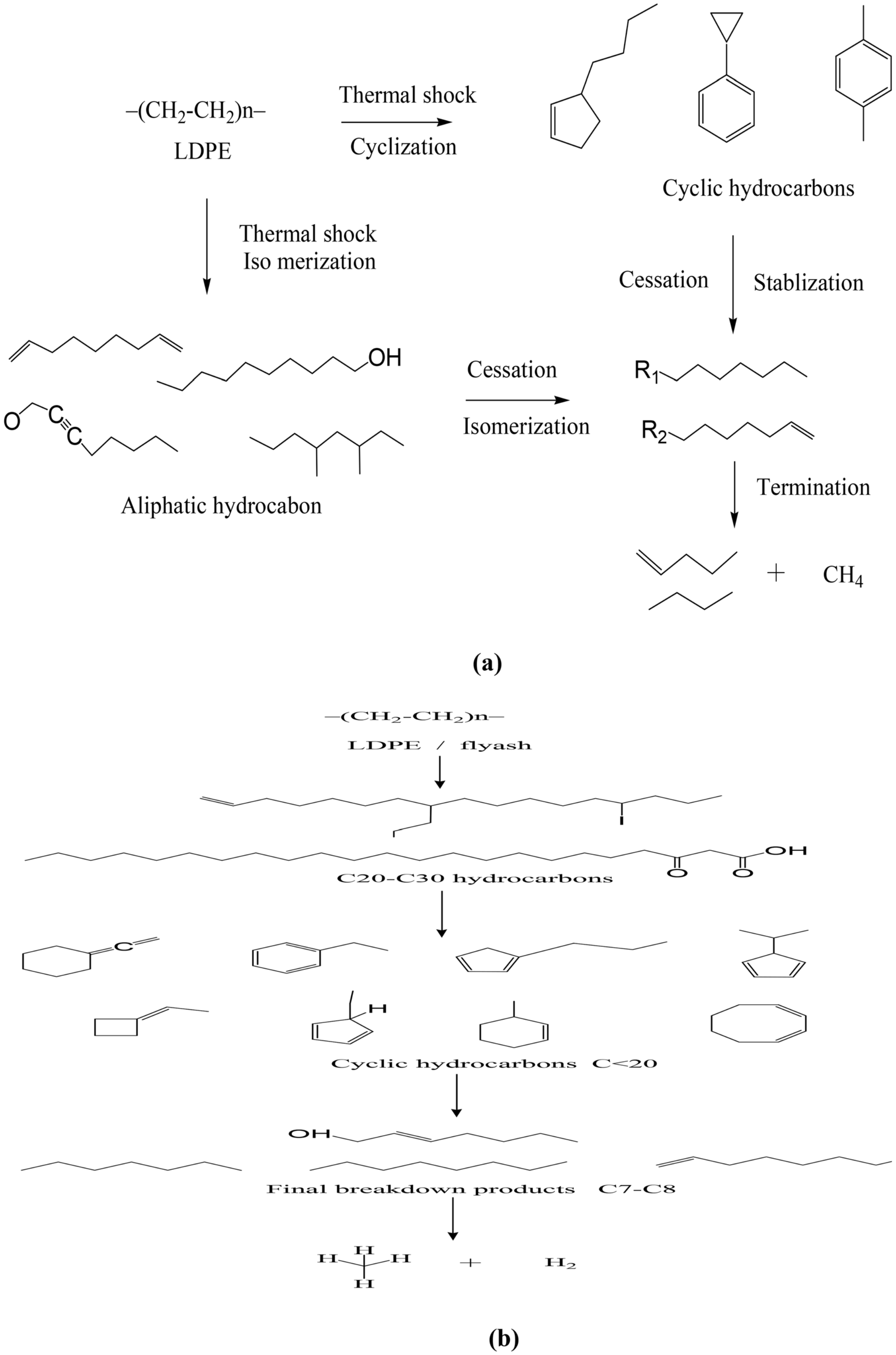

Fig. 15 (a) Possible reaction mechanism for LDPE thermal pyrolysis (b) catalytic pyrolysis over fuel oil fly ash catalyst.

500 °C and solidifies at room temperature which is not useful for further applications which is the reason why one has to spend more energy and time to achieve the required temperature more than 500 °C to get thin liquid oil. Further liquid production also decreases at high temperature, which has been already discussed in the non-catalytic part of this

paper. Mostly fossil fuels such as coal or furnace oil are used to get energy in Pakistan, which increases the pollution level in the forms of NOX, SOX, CO_2 and particulate matter. So catalytic pyrolysis has potential environmental benefits. Jianchen Lai *et al.* performed the catalytic pyrolysis of plastic with fly ash and non-catalytic pyrolysis of plastic and reported the same environmental benefits.[86]

4. Conclusions

Catalytic pyrolysis of waste LDPE is a promising technique to convert waste LDPE into liquid and other useful by-products, using a fuel oil fly ash catalyst. This study investigated the potential of fuel fly ash as a catalyst in catalytic pyrolysis of waste LDPE to produce kerosene fuel range hydrocarbons and valuable gases such as CH_4 and H_2. The thermal pyrolysis of LDPE produced mainly aromatic hydrocarbons and long chain aliphatic hydrocarbons with higher viscosity. However, the addition of the fly ash catalyst promoted the alkane and short chain hydrocarbon production such as heptane, octane, and others. The percentage of alkanes and CH_4 and H_2 yields were found to be enhanced with the increasing percentage of fly ash catalyst in the experiments. The selectivity of kerosene (C7–C16) and diesel (C16–C23) fractions reached up to 68 wt% and 29wt% at the highest ratio of the fly ash catalyst respectively. The results of GC/MS are supported by nuclear magnetic resonance. Moreover, physicochemical analysis revealed that the flash point and GCV of catalytic pyrolysis oil samples are comparable to those of conventional diesel. In addition to liquid and gaseous products, char has also been found to be a useful solid product for energy applications as it has a heating value that is comparable to some varieties of coal. Considering the quality of pyrolysis products and the catalytic performance of fly ash as a catalyst, it can be inferred that catalytic pyrolysis of LDPE could be a promising approach to manage plastic and fly ash waste and produce energy simultaneously achieving a win–win situation. This can potentially promote a circular economy and conserve the environment.

Conflicts of interest

There are no conflicts to declare.

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