

Spectroscopic Analysis of Pp and Pet Pyrolysis Oils: A Promising Alternative to Fossil Fuels.

Nurudeen A.,^a Nwosu F. O.,^a Ibukun O. J.^b and Doluwamu A. P.^a

^aDepartment of Industrial Chemistry, Faculty of Physical Science, University of Ilorin, Nigeria.

^bDepartment of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur-741246, West Bengal, India.

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ABSTRACT

In order to evaluate the potential of pyrolyzed oil as a substitute and renewable energy source, this study investigates the physical, chemical, and spectroscopic characteristics of pyrolyzed oil with those of conventional fuel. The aim is to establish spectroscopic properties and compare the physico-chemical properties of pyrolyzed oil with ordinary fuel. Diesel fuel, polypropylene (PP) oil, and polyethylene terephthalate (PET) oil were the materials used in this investigation. The physico-chemical properties test carried out on the samples were, density, viscosity, flash and fire point, cloud and pour point, and also cetane number. The Fourier-Transform Infrared spectroscopy (FTIR) and the Gas Chromatography-Mass Spectroscopy (GC-MS) analysis were the spectroscopic properties that were tested. The results derived from the physico-chemical properties test shows that the PP oil exhibited a density of 1.288g/ml and a high viscosity of 884.9 cSt at 27.6°C. In contrast, PET oil displayed a higher density of 1.445 g/ml but significantly lower viscosity at 211.9 cSt at 27.7°C. PP oil exhibited a lower flashpoint (44°C) and fire point (49°C) than Diesel fuel. PET oil demonstrated similar trends with a flashpoint of 59°C and a fire point of 62°C. However, PET oil's cloud point (25°C) and pour point (21°C) were closer to Diesel fuel's typical values. The cetane number revealed that both sample oils, PP (60.38) and PET (58.33), possessed higher cetane numbers than the ASTM standard range for Diesel fuel. Comparing the properties, it is clear that plastic PP and PET oils are denser and more viscous. They exhibit some favourable properties, however, their flammability characteristics require careful consideration for safety. The findings suggest that PET oil may be a

more promising candidate for specific applications with its lower viscosity and better cold weather performance.

Keywords: Pyrolyzed oil, Conventional fuel, Physico-Chemical and Spectroscopic Properties

I. INTRODUCTION

As the world's population grows, the economy expands quickly, cities continue to rise, and lifestyles change, plastic trash production and consumption are rising alarmingly. The daily creation of plastic waste also increases the brief lifespan of plastic. Current annual global plastic manufacturing could reach 300 million tons (Ratnasari et al., 2017; Miandad et al., 2016a). The petrochemical hydrocarbons used to create plastics have additives like flame retardants, stabilizers, and oxidants that hinder biodegradation (Ma et al., 2017). Recycling of plastic trash can be done in various methods, although in most developing nations, open or landfill disposal is the norm for managing plastic waste (Gandidi et al., 2018). The landfilling of plastic garbage creates a home for insects and rodents that may spread various diseases. Also, the cost of labour, maintenance, and transportation may raise the price of a recycling operation (Gandidi et al., 2018). In addition, the amount of land needed for landfills is decreasing, particularly in cities, due to rising urbanization. One popular method for converting plastic trash into energy in the form of solid, liquid, and gaseous fuels is pyrolysis.

Pyrolysis is one of the practical methods for turning plastic waste into fuel. An organic substance is depolymerized during pyrolysis, a complicated series of thermal and chemical events that occur without oxygen. Plastics must be heated to a high temperature as part of the process, and the

2.1 Reagents, Apparatus and Instruments

The list of apparatus includes the following: Beakers, Measuring cylinders, Stirrers, Thermometers, Weighing balance, and standard apparatus normally used in a chemical laboratory. The list of reagents includes the following: Red dye, n-hexane, Distilled water, and Ethanol. The list of instruments includes the following: FTIR spectrometer and GC-MS spectrometer, Analytical balance, Viscometer, Digital densitometer, Closed-cup flash point tester.

2.2 Characterization of PET and PP pyrolyzed oil as fuels

The pyrolyzed oil was characterized in order to compare the properties of pyrolyzed oil with those of diesel(standards); various. Various tests were carried out in the laboratory under various testing conditions, and later, a comparison was made. The tests that were performed are Colour, Density, Viscosity, cetane number, Flash Point, Fire point, Cloud Point, Pour Point, FTIR, and GC/MS (GC/MS - Gas chromatography / Mass Spectroscopy).

2.3 Physicochemical Analysis

(a) Density

A density bottle was used to carry out the measurement of density, specific gravity and API gravity. A density bottle that has been washed and rinsed with distilled water and oven-dried was used to determine the density of PET and PP oil. Research have shown that liquid oil from high-density polyethylene and low-density polyethylene has high caloric values similar to the oil obtained from coal and wood (Sogancioglu et al. 2017). The weight of the empty density bottle was weighed on a weighing balance at a specific temperature and noted. A 20 ml of fuel was poured into the density bottle and was weighed at the same temperature, the weight of the empty bottle was subtracted from the present weight (empty bottle + bottle with oil) to obtain the weight of the oil, the weight of the oil was now divided by the volume of oil to get the density.

(b) Viscosity

The viscosity of this fuel can be used to assume how heavy or the kinetics of the flow of this fuel; fuels of high densities are known to be viscous and of high chain of hydrocarbon, while hydrocarbon of less viscosity are less viscous with less force of attraction between the carbon atoms compared to the high-density fuels. Low-density fuels or low viscous fuels are more volatile as such with greater kinetics. Ostwald viscometer was

used. The viscometer was washed and calibrated with distilled water. The temperature of the room was taken. The fuel was introduced into the viscometer and was adjusted (suck) to a point in the capillary arm about 5mm ahead of the first timing mark. The fuel was left to flow freely and the time required for the meniscus to pass from the first mark to the second mark was recorded.

(c) Pour point (ASTM D5853-16)

The fuel was poured to the level mark into a test jar having a cork holding a thermometer. The oil was heated without stirring to 9°C above the expected pour point (or 45°C whichever is higher) in a bath maintained at 12 °C above the expected pour point (or 48°C whichever is higher). The test jar was transferred to a water bath maintained at a lower temperature to cool the sample and was observed for pour point. Care was taken not to disturb the oil, as paraffin wax crystals were formed after cooling the oil. The jar was then tilted to check for movement of the oil. If the oil still flows when its temperature reaches 27°C the jar was transferred from one bath to another with a lower temperature until the oil in the test jar does not flow when tilted. The jar was then held in a horizontal position for 5 seconds. If the oil shows any movement, the test jar was replaced in the jacket and the test was repeated for flow at the next temperature 3°C lower. This was continued until the oil in the jar does not move and temperature was reported as the pour point.

(d) Flash point and fire point (ASTM D56-97a)

The fuel sample was poured into a cup. Thermometer was placed in the oil and the oil was heated. The test flame was passed over the cup at every 2°C increase in the oil temperature. The flash point temperature was reached when the sample vapors ignited momentarily in air. When the sample vapors sustained combustion at least five seconds, the fire point temperature was reached.

2.4 Instrumental Analysis

The analysis using instruments are as follows:

a) Gas chromatography and mass spectroscopy (GC-MS):

The GC-MS analysis of all the oils produced was performed on a Hewlett Packard 5972 mass spectrometer operated at ionization energy of 70eV linked to an HP-5890 gas chromatograph, with a splitless injector (at 250°C), fitted with a flexible silica capillary column of 30m x 0.32mm internal diameter; 1.0µm film thickness. A 1µL of each sample was injected by an

autosampler; the oven temperature was programmed from 40 to 350°C at a rate of 4°C/min and held at 300°C for 20min, using helium, carrier gas at a flow rate of 1ml/min. The samples were run using full scan and single ion monitoring (SIM) and were recorded using the HP chem station system (Odebunmi and Ismaeel, 2013).

b) Fourier Transformation Infrared Spectroscopy (FTIR)

FTIR of the pyrolysed oil obtained was taken in a Perkin-Elmer Fourier transformed infrared spectrophotometer with resolution of 4 cm⁻¹, in the range of 400-4000 cm⁻¹ using Nujol mull as reference to know the functional group composition.

III. RESULTS

3.1 Physico-chemical properties of PP and PET in Comparison with ASTM Standard

In terms of colour, both Polypropylene and PET oils exhibit yellowish hues, indicating the influence of organic compounds originating from their pyrolyzed plastic precursors. In comparison to Diesel fuel, which also has an amber colour, the colour of the sample oils may appear somewhat similar. However, Diesel fuel generally tends to have a broader range of colouration, encompassing

a spectrum from light to dark amber (Standard Specification for Diesel Fuel, n.d.).

Polypropylene (PP) oil exhibited a 1.288 g/ml density and a high viscosity of 884.9 cSt at 27.6°C. In contrast, Polyethylene terephthalate (PET) oil displayed a higher density of 1.445 g/ml but significantly lower viscosity at 211.9 cSt at 27.7°C (Standard Specification for Diesel Fuel, n.d.). These values were compared with the ASTM standard for Diesel fuel, demonstrating that both sample oils diverged significantly from the typical Diesel fuel density and viscosity ranges (Table 1).

Also, Polypropylene oil exhibited a lower flash point (44°C) and fire point (49°C) than Diesel fuel. PET oil demonstrated similar trends with a flash point of 59°C and a fire point of 62°C. These results suggested a higher flammability risk for both sample oils compared to Diesel fuel. However, PET oil's cloud point (25°C) and pour point (21°C) were closer to Diesel fuel's typical values, indicating potential advantages in cold weather performance (Table 1). The cetane number, an indicator of ignition quality, revealed that both sample oils, Polypropylene (60.38) and PET (58.33), possessed higher cetane numbers than the ASTM standard range for Diesel fuel (Table 1). This characteristic suggested efficient combustion and ignition properties for both sample oils (Standard Specification for Diesel Fuel, n.d.).

Table 1: Comparison of physical properties of PP and PET oil samples with Diesel fuel

Property	PP OIL	PET OIL	ASTM STANDARD FUEL
Colour	Amber yellow	Pale yellow	Light amber to Dark amber
Density (g/cm ³)	1.288	1.445	0.82 to 0.85 g/cm ³
Viscosity (cSt)	884.9 at 27.6°C	211.9 at 27.7°C	2.0 to 4.5 cSt at 40°C
Flashpoint (°C)	44	59	> 52°C (minimum ASTM D93)
Fire point (°C)	49	62	> 55°C (minimum ASTM D92)
Cloud point (°C)	29	25	-11 to -6°C
Pour point (°C)	26	21	6 to -12°C
Cetane number	60.38	58.33	> 40 (ASTM D613)

3.2 FTIR ANALYSIS

3.2.1 FTIR Analysis of Polypropylene (PP) Oil

In PP oil, several distinctive peaks in the polypropylene oil's FTIR spectra have been found. Particularly, the peaks at within range of 3821-3957cm⁻¹ are a sign of aliphatic C-H stretching vibrations, which imply the existence of aliphatic

hydrocarbon chains in the oil generated from polypropylene. This is consistent with the predicted pyrolyzed polypropylene composition, which is largely composed of hydrocarbons. Moreover, the O-H stretching vibration is associated with the peak at 3431.66 cm⁻¹, which denotes the existence of hydroxyl (OH) groups. These hydroxyl groups may

have developed during the pyrolysis process or they may have come from residual moisture, other oxygen-containing compounds, or the feedstock itself. Carbonyl (C=O) stretching vibrations make up the peak at 1734.79 cm^{-1} , which suggests the existence of carbonyl functional groups. This might indicate that the polypropylene oil contains ketones or aldehydes, which could be byproducts of heat breakdown. In addition, the peak at 1639.12 cm^{-1} is connected to a conjugated C=C bond, suggesting that the polypropylene oil may include aromatic chemicals. The presence of aromatic chemicals in the pyrolyzed oil may have an impact on its combustion properties since they are recognized for their stability and resistance to pyrolysis. Using Diesel fuel as a comparison, it can be shown that Diesel often includes a combination of aliphatic hydrocarbons with different chain lengths and branching, leading to distinctive peaks in the FTIR spectrum that are comparable to those seen in Polypropylene oil. Yet, because carbonyl or conjugated C=C bonds are less frequent in diesel fuel, it's possible that diesel fuel does not show peaks associated with these structures. Nevertheless, because these functionalities are less frequent in ordinary Diesel fuel, diesel fuel may not show peaks associated with carbonyl or conjugated C=C bonds (Nespeca et al., 2018).

3.2.1 FTIR Analysis of Polyethylene Terephthalate (PET) Oil

In PET oil, by contrasting this data (Figure 3) with typical FTIR spectra of diesel fuel, we can make some educated guesses about the chemical composition and functional groups present in both samples. Several peaks in the FTIR spectrum of PET oil point to functional groups containing oxygen. Peak near 3455.57 cm^{-1} is in accordance with O-H stretching vibrations, which may point to the presence of substances containing hydroxyl groups, such as alcohols or phenols. A peak at 1739.31 cm^{-1} is also associated with a carbonyl C=O stretching vibration, which is frequently observed in esters or ketones. Peaks near 736.37 cm^{-1} have been linked to C-O stretching vibrations, which may suggest the presence of ethers. On the other hand, diesel fuel typically has a different combination of functional groups. The aliphatic (alkane) hydrocarbons (alcohols), aromatic (aromatic C=C stretching), and carbonyl groups tend to have peaks in the FTIR spectrum of diesel fuel. Diesel fuel is a hydrocarbon, as evidenced by the lack of strong O-H stretching vibrations seen in the PET oil spectrum. Furthermore, the region between 2941.00 and 2864.60 cm^{-1} of diesel fuel frequently exhibits alkane C-H stretching vibrations (Nespeca et al., 2018).

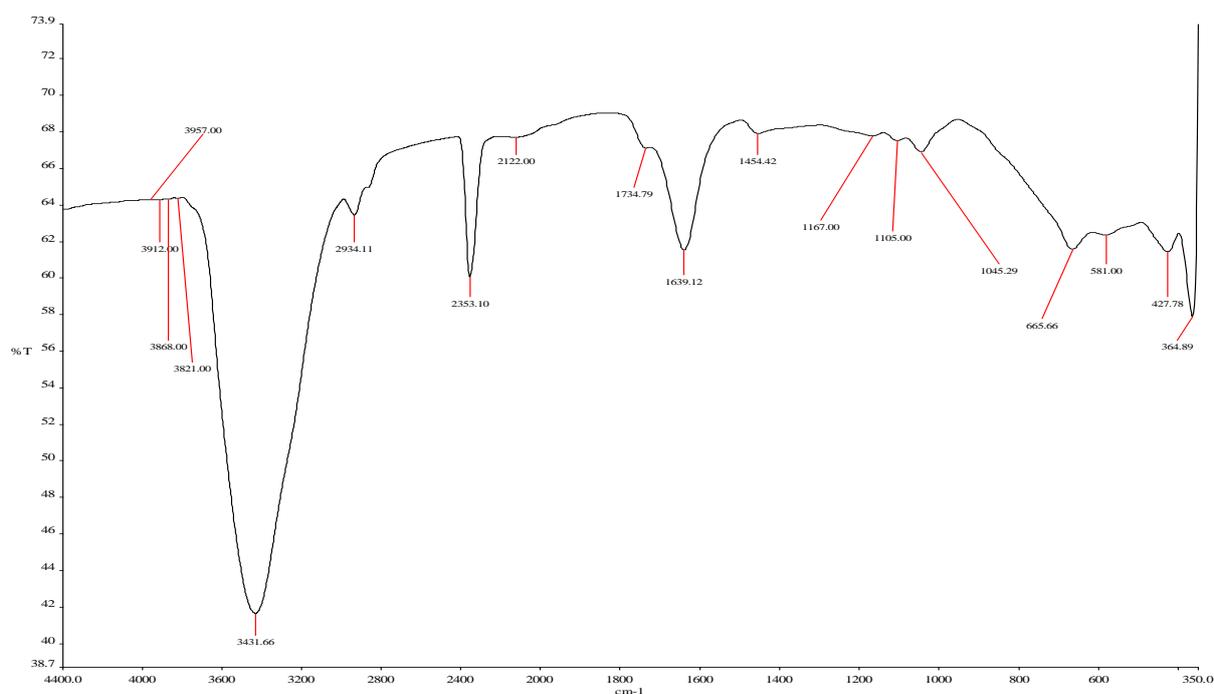


Figure 2: FTIR spectra of PP Oil

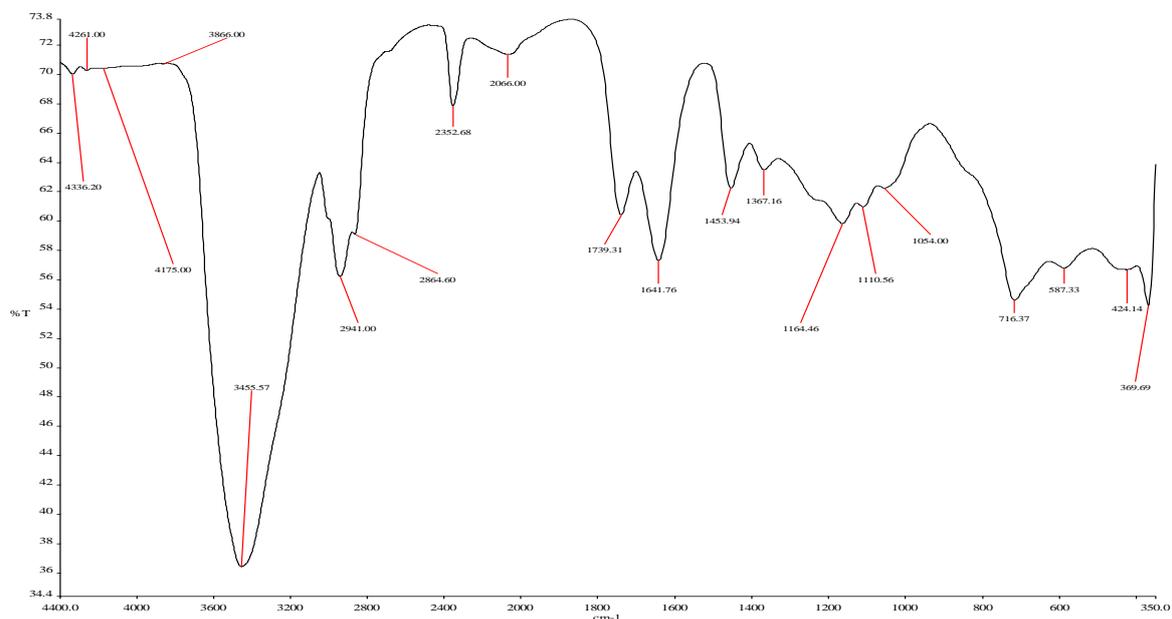


Figure 3: FTIR spectra of PET Oil

3.3 GC-MS ANALYSIS

3.3.1 GC-MS Analysis of PP(Polypropylene) Oil

Polypropylene oil's GC-MS analysis produced a wide variety of compounds, demonstrating the complexity of its chemical composition. Figure 4 depicts the GC-MS spectra of PP oil. Several distinct peaks were found, each corresponding to a different compound in the oil. Various hydrocarbons, compounds containing oxygen, and other chemical species were notable compounds found in polypropylene oil, which was a pyrolyzed plastic product. The complex chemical composition of polypropylene oil was revealed by the identification of several hydrocarbon- and ester-related chemical compounds. We noted the presence of a variety of alkanes and alkenes, which are typical components of fuels derived from hydrocarbons, among the hydrocarbon-related compounds. Octane, nonane, and decane were notable hydrocarbons with straight-chain aliphatic structures. The overall diversity of hydrocarbons in Polypropylene oil was also increased by the discovery of a few branched alkanes, including iso-octane. Esters were also found in the Polypropylene oil sample in addition to hydrocarbons. Esters are compounds that contain oxygen and are created when an alcohol reacts with an organic acid. These esters, which are a part of the oil's intricate chemistry, included methyl butyrate and ethyl acetate in this analysis. These esters might have been created when plastic polymers were broken down during the pyrolysis process, creating ester functional groups in the resulting oil. Additionally, the presence of

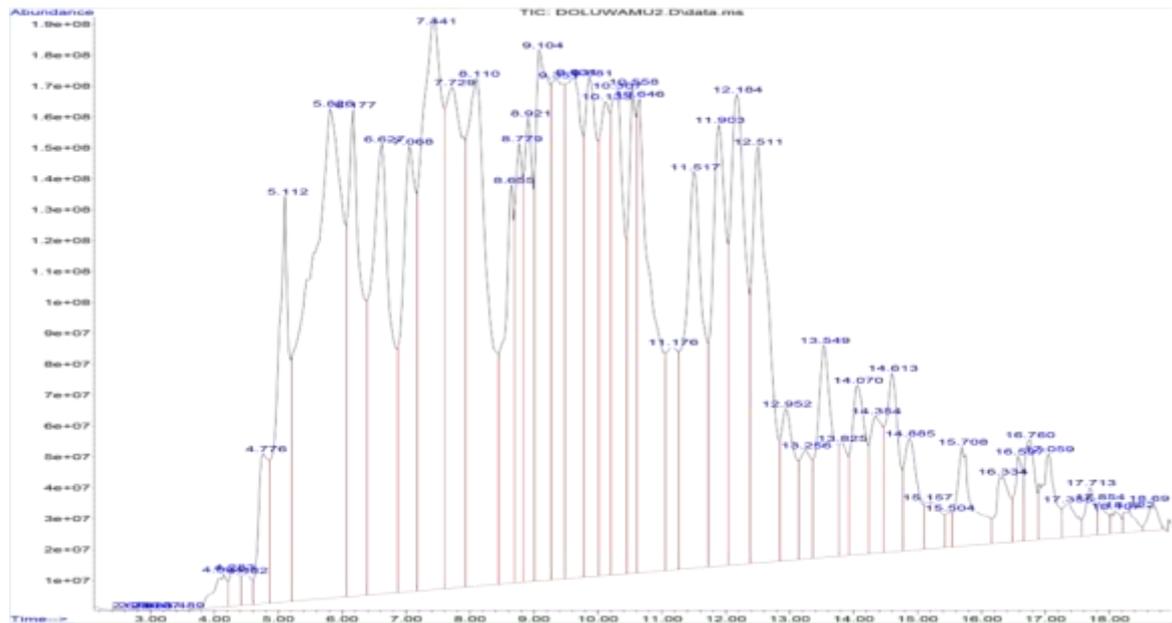
substances like 2-ethylhexyl acetate and isobutyl isobutyrate suggests that branching and isomerization reactions may have played a role in the formation of esters in polypropylene oil. These substances increase the variety of esters already present and imply a complicated reaction pathway during the pyrolysis of plastics like polypropylene. According to its typical hydrocarbon nature, diesel fuel's composition was distinguished by the absence of functional groups that contained oxygen. The comparison of diesel fuel and polypropylene oil revealed significant variations in their chemical structures. Alcohols and esters, which are oxygen-containing compounds, were found in polypropylene oil but conspicuously absent from diesel fuel. These results imply a more complex and oxygen-rich molecular structure in polypropylene oil, which is produced by the pyrolysis of plastic waste.

3.3.2 GC-MS Analysis of PET(Polyethylene terephthalate) Oil

PET oil underwent GC-MS analysis, which identified a wide variety of substances, including esters and hydrocarbons (Figure 5). In the GC-MS analysis, hydrocarbons were discovered that are present in both PET oil and diesel fuel. These substances are essential to the combustion of fuel. Alkanes, alkenes, and aromatic hydrocarbons are typical hydrocarbons found in both diesel and PET oil. The PET oil contains esters, which are organic molecules with carbonyl (C=O) and oxygen (O) functional groups. Esters are unusual to find in diesel fuel. They may have

gotten into PET oil due to the breakdown of PET plastic during pyrolysis, which can result in the formation of compounds with ester groups. Compared to diesel, PET oil contains a wider range of substances because it contains hydrocarbons and esters produced when plastic polymers break down. The main component of diesel fuel is hydrocarbons, which are well-known for having

excellent combustion characteristics. PET oil, on the other hand, might have a different combustion profile because ester compounds are present (Hsu, n.d.). Esters in PET oil could affect how well it burns and what kind of emissions it produces. More investigation is required to comprehend how these esters affect PET oil's efficiency as a fuel.



IV. DISCUSSION

Polypropylene oil, resulting from the pyrolysis of polypropylene plastic waste, exhibits unique physical properties. It possesses a higher density than Diesel fuel, which can be attributed to the complex and heavier compounds formed during pyrolysis. The exceptionally high viscosity of Polypropylene oil makes it significantly more viscous than both PET oil and Diesel fuel, presenting challenges in terms of fluid flow and lubrication. Its lower flash and fire points raise concerns about flammability and safety. While it has commendable cold weather performance, its high viscosity may limit its application in low-temperature environments. The remarkable cetane number of Polypropylene oil suggests excellent ignition quality for combustion (Table 1).

PET oil, derived from the pyrolysis of polyethylene terephthalate plastic, displays its own distinctive set of physical properties. It boasts a higher density compared to Diesel fuel, primarily due to the presence of complex and heavier compounds. PET oil exhibits lower viscosity than Polypropylene oil but remains more viscous than Diesel fuel. With higher flash and fire points than Polypropylene oil, PET oil is a safer option in terms of flammability. Its superior cold weather performance, characterized by lower cloud and pour points, makes it better suited for applications in colder climates. PET oil maintains a commendable cetane number, indicating efficient combustion capabilities (Table 1).

The FTIR examination of polypropylene oil shows the presence of aliphatic hydrocarbons, carbonyl groups, and perhaps conjugated C=C bonds, indicating a complex composition that may be different from standard diesel fuel. These variations in chemical composition call for more research, especially in terms of combustion characteristics and emissions, since they may have ramifications for polypropylene oil's viability as an alternative fuel source (Figure 2). As a result of its pyrolyzed origin from plastic waste, PET oil is likely to contain oxygen-containing functional groups, according to the FTIR analysis, whereas diesel fuel primarily consists of hydrocarbon compounds with little oxygen content. The chemical difference in functional groups may affect these fuels' performance and combustion characteristics, as well as their effects on the environment (Figure 3). A more thorough understanding of the chemical compositions and characteristics of the specific compounds present in each sample would be possible with further in-depth analysis and quantification.

The GC-MS analysis of polypropylene oil (Figure 4) revealed significant chemical compositions of the oil with a wide variety of compounds, including functional groups that contain oxygen, although this complexity may have an impact on combustion and emissions characteristics. Also, the GC-MS analysis of Polyethylene Terephthalate (PET) oil (Figure 5) has shed important light on the chemical composition of the substance, emphasizing the presence of both hydrocarbon and ester compounds. The unique composition of PET oil is highlighted by comparing these results to diesel fuel, which may have an impact on its suitability as an alternative fuel source. Given its unique chemical composition, more research is necessary to fully evaluate the combustion characteristics and environmental impact of PET oil in comparison to diesel fuel. It is essential to understand these differences to determine PET oil's potential as a sustainable and practical fuel option.

V. CONCLUSION

As a result of this thorough evaluation, PET and Polypropylene oils are highlighted for their versatility as possible Diesel fuel substitutes. The complex chemical composition of these oils was revealed by FTIR and GC-MS analyses, which are characterized by hydrocarbons, esters, and compounds containing oxygen. The physical property tests demonstrated their unique physical characteristics, such as greater density, variable viscosity, lower flammability, improved cold weather performance, and improved ignition quality when compared to diesel fuel. These plastic-derived oils do not, however, come without difficulties. For particular applications, they need to be carefully considered due to their high viscosity and flammability. PET oil stands out as a more promising contender thanks to its favorable viscosity profile and superior cold weather performance. However, both oils need more investigation and improvement to be tailored for particular industrial applications, minimizing their drawbacks and maximizing their benefits. Ultimately, this research offers important new information about how PET and Polypropylene oils might be used as Diesel fuel substitutes. These results highlight the need for a careful strategy in the search for more efficient and sustainable energy sources and chemical feedstocks, taking into account the particular characteristics and composition of these oils. Realizing the full potential of these oils derived from plastic in addressing the complex issues facing our energy

landscape and environmental sustainability will require more research and innovation.

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