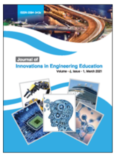

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Effect of plastic pyrolysis oil and its blends with diesel on cetane index

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Abstract

Availability and higher gasoline price have attracted the attention of researchers towards alternative fuels. Plastic is produced from the byproduct of gasoline products, which possesses a higher possibility of recycling the waste plastic as an alternative fuel. Research conducted on plastic fuel shows that a diesel engine can run with 100% plastic oil. The present work is focused on the effect of distilled plastic oil on the cetane index as the cetane index is a major fuel property of diesel that affects the ignition quality and exhaust emissions of the engine. For the measurement of the cetane index, two standards are followed and they are ASTM D4737 and ASTM D976. It is found that Crude plastic oil produced from thermal pyrolysis of waste plastic possesses a wide variety of hydrocarbon i.e. lower to higher hydrocarbon. From the fractional distillation of crude plastic oil at three temperature ranges 200°C, 290°Cand up to the final boiling point, it gave petrol grade oil and diesel grade oil (both low and high grade). Also, it was found that the recovery of distilled high-grade plastic oil is higher than other distilled crude plastic oil. Along with this, crude plastic oil, as well as high-grade plastic oil, have a higher cetane index than the diesel available in the market. Similarly, blending diesel with high-grade plastic oil up to 20% by volume and with low-grade plastic oil up to 10% by volume increases the cetane index of fuel.

Abbreviations and acronyms

CI : Cetane Index
CN : Cetane Number
HGPO : High Grade Plastic Oil
LGPO : Low Grade Plastic Oil
DCN : Derived Cetane Number
5LGPO : Blend of LGPO with diesel 5% by volume
10HGPO : Blend of HGPO with diesel 10% by volume
10LGPO : Blend of LGPO with diesel 10% by volume
15HGPO : Blend of HGPO with diesel 15% by volume
20HGPO : Blend of HGPO with diesel 20% by volume

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1. Introduction

Plastics are made from natural and organic materials mostly by crude oil. Petroleum products such as naphtha, gasoline, diesel, kerosene, and lubricants are obtained by employing the crude oil to fractional distillation chamber in an oil refinery. Plastics are generally made from the residue of fractional distillation. Recycling plastic is a usable process for converting products formed from petroleum waste into more useful products such as gasoline, diesel, kerosene, and heavy oil [1]. Plastic waste is one of many types of wastes that take too long to decompose. Normally plastic takes up to 1000 years to decompose in landfills areas. The major landfilling sites aren't only hampering the quality of land but also creating a harmful effect on human beings as well as on animals. The increasing consumption of petroleum products leads to the shortage of crude oil and there is uncertainty in the price of crude in the international market which affects the national economy

[2].

Pyrolysis is a thermochemical process that occurs when the amount of oxygen required for complete combustion is significantly low or in the absence of oxygen [1]. There are two types of pyrolysis, one is thermal pyrolysis and another is catalytic pyrolysis. Thermal pyrolysis means employing heat directly to the furnace and condensing the vapor while catalytic pyrolysis is passing the vapor from the furnace to the catalyst and condensing the vapor. Thermal Pyrolysis processes are classified into three classes, low, medium, and high temperatures pyrolysis based on the temperature range used to destroy plastic structure [3]. The temperature corresponding defining the pyrolysis states are, for low thermal pyrolysis temperature ranges less than or equal to 600°C, while for medium thermal pyrolysis temperature range is 600–800°C and for high-temperature thermal pyrolysis, the temperature is greater than 800°C [4]. The products obtained from the thermal pyrolysis of plastics depend on many factors. Some of the factors are the type of plastics feed, temperatures employed, feeding chamber arrangement, pyrolysis time, reactor type, and condensation unit arrangement [5, 6]. Pyrolysis performed at low-temperature favors liquid products production and pyrolysis performed at high-temperature favors gaseous products. With the rise of temperature from 460°C, the yield of gases increases significantly. Thermal pyrolysis of various types of plastics at 600°C yields a mixture of hydrocarbon gas consisting of alkane, alkadines, and alkenes with carbon number up to C53 [7]. Thermal pyrolysis of plastic waste produced maximum crude plastic oil which is 80.8%, non-condensable gases 13%, and char 6.2%, while catalytic pyrolysis of plastic waste decreased the crude plastic oil yields to 54% for natural zeolite and 50% for synthetic zeolite [8].

Cetane number is one of the important fuel properties which shows the ignition quality of fuel. Accurate measurement of cetane number is a difficult process that requires a special Cooperative Fuel Research (CFR) engine where the test is performed under a standard test condition. For calculation of cetane number, a mixture of hydrocarbon which includes cetane (hexadecane) and isooctane (2, 2, 4, 4, 6, 8, 8-heptamethylnonane) is determined by gas chromatography and mass spectrometry. This hydrocarbon affects the ignition delay of the engine [9]. Determining cetane number requires a complex test engine and highly skilled operators which is a costly method. As an alternative to cetane number, a correlation method was used in the late 1990s where derived cetane number was measured on a constant volume combustion chamber [10, 11]. Instead of measuring cetane number, ignition delay and ignition timing were measured by the constant volume combustion chamber. Software of ignition quality tester converted the value of ignition delay and ignition timing into derived cetane number [12]. Blends of cetane number improvers such as 2-ethylhexyl nitrate, 2-methoxyethyl ether, and cyclohexyl nitrate having high cetane number when used with diesel shorten the ignition delay, reduces the NOx emission, increases the cylinder pressure and net heat releases but increases the HC and CO concentration [13, 14].

In the alternative of cetane number, determining the cetane index is an easy and cheap method. Cetane index is calculated by using two fuel properties i.e. density and distillation range of the fuel. There are various methods for determining the cetane index based on the imperial unit used and how many distillation points are used. Commonly used methods are: ASTM D4737, which uses density and distillation recovery at 10% 50%, and 90% of the sample, and ASTM D976, which uses density and distillation recovery at 50% of the sample [15].

Crude plastic oil composes hydrocarbon from shorter chain to longer chain, aromatic hydrocarbon, cycloalkanes, olefins, and organic compounds. The crude oil is allowed to fractional distillation at three temperature ranges i.e. 200°C, 290°C, and up to the final boiling point. Distilled plastic oil up to 290°C is regarded as High-grade plastic oil (HGPO) and from 290°C to final boiling point as low-grade plastic oil (LGPO) and their corresponding blends with diesel as blends of high-grade plastic oil with diesel (BHGPO) and blends of low-grade plastic oil with diesel (BLGPO). Volumetric blending was performed to blend the HGPO and LGPO with diesel. Effects of the blends of HGPO and LGPO on the cetane index are investigated by following two standards i.e. ASTM D976 and ADTM D4737.

2. Material and methods

2.1. Crude oil production

Crude plastic oil is produced in a one kg batch reactor at a temperature of 450°C. The crude oil contains some fraction of char. The crude oil is allowed to pass through a sinter glass setup of filtration to remove unwanted char from the crude oil. One kg batch reactor for thermal pyrolysis is shown in Figure 1.

2.2. Fractional distillation

Fractional distillation by ASTM D86.

- The initial boiling point (IBP) is the temperature measured in thermometer at which the first drop of condensed vapor coming from the lower end of the condenser tube is noted. Lower IBP shows the presence of lower hydrocarbon in the sample.

Figure 1: Pyrolysis batch reactor.

- The final boiling point (FBP) is the temperature in the thermometer at which the temperature starts to drop in the thermometer despite increasing heat.
- Percent evaporated is the sum of the percent of vapor recovered and vapor trapped in the cooling unit. Lower cooler unit temperature leads to condense the higher hydrocarbon in the cooling tube, which leads to blocking the cooling pipe.
- Percent recovered is the volume of condensate vapor collected in the receiving cylinder.

Fractional distillation of 100ml sample was performed in an apparatus where the thermometer was placed at the top of the apparatus fitted with a cork. The blub of the thermometer was placed just above the neck of the apparatus. The neck of the apparatus leads towards the cooling channel. From the neck of the apparatus hot vapor passed to the cooling chamber, where the vapor was cooled with the help of a chiller. After noting the IBP, recovery of the condensed vapor was noted for every 10°C till the FBP. The setup of fractional distillation is shown in Figure 2.

Figure 2: Distillation setup

2.3. Cetane index calculation

Cetane index is an indicator of the ignition quality of diesel in an internal combustion engine which can be calculated from density and distillation data. One of the very popular techniques of fractional distillation is ASTM D86 and Density at 15°C is D1298. There are various methods for determining the cetane index of diesel. One of the methods is ASTM D976, where CI is calculated by the results obtained from the density at 15°C and mid-boiling temperature of the sample, and another method is ASTM D4737 which contains four variables. In this method of calculating the cetane index, density and distillation recovery temperatures of 10%, 50%, and 90% of the fuel are used.

- ADTM D4737 provide the four variable equation presented in Equation 1 [16].

$$\begin{aligned} \mathrm{CI} &= 45.2 + 0.0892 T10N \\ &+ (0.0131 + 0.901 B) T50N \\ &+ (0.0523 - 0.420 B) T90N \\ &+ 0.00049[(T10N)^2 - \\ &(T90N)^2] + 107B + 60B^2 \end{aligned} \tag{1}$$

Where,

CI : Calculated Cetane Index

D : Density at 15°C, g/cm^3

DN : D - 0.85

B : exp[-3.5DN -1]

T10 N : T10 - 215

T50 N : T50 - 260

T90 N : T90 - 310

T10 : Distillation temperature (°C) corresponding to 10% (V/V) recovery

T50 : Distillation temperature (°C) corresponding to 50% (V/V) recovery

T90 : Distillation temperature (°C) corresponding to 90% (V/V) recovery

- ASTM D976 provide two variable equation which is presented in Equation 2 [17].

$$\begin{aligned} CCI &= 454.74 - 1641.416 D \\ &+ 774.74 D^2 - 0.554 T50 \\ &+ 97.803[\log (\mathrm{T50})]^2 \end{aligned} \tag{2}$$

Where,

CCI : Calculated Cetane Index

D : Density at 15°C, g/cm^3

T50 : mid-boiling temperature, °C

3. Result

Thermal pyrolysis of waste plastic is done at 450°C. The yield of the crude oil varies from 70-90% depending upon the type of plastic. The crude oil contains paraffin, petroleum, diesel, kerosene, lubricant, and waxes hydrocarbon. The presence of waxes and impurities creates problems in distillation, the crude oil is allowed to pass through filtration so that amount of waxes and impurities are reduced. Fractional distillation is done at 200°C, 290°C, and 360°C. The initial boiling point and final boiling point are noted to contain wax materials. Recovery of distilled oil is recovered at every 10°C.

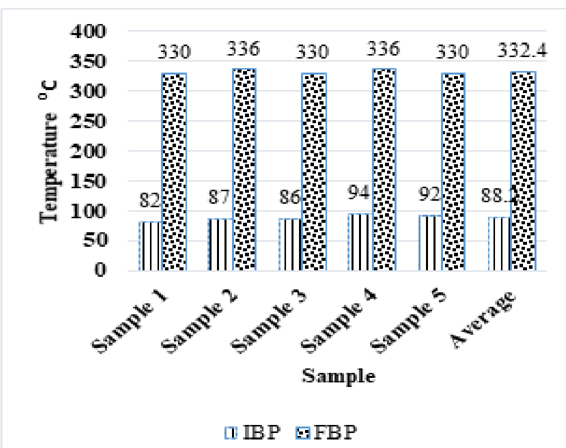

Figure 3: IBP and FBP of crude oil in (°C)

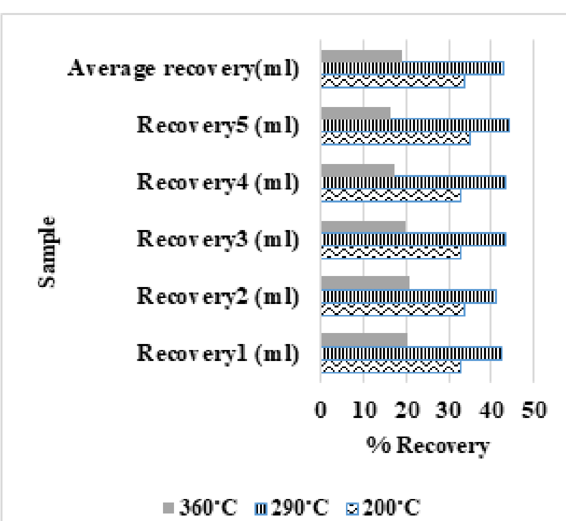

Figure 4: Distillation recovery of crude oil in ml

From Figure 3, it can be observed that lighter hydrocarbon is present in crude plastic oil as the range of the initial boiling point of crude oil is 80-90°C. The crude oil contains heavier hydrocarbon as the final boiling point of crude oil is 330°C to 336°C. So crude plastic oil is a mixture of both the higher and lighter hydrocarbon.

The distillation range of diesel is 240-360°C [18] Fractional distillation is allowed at three different temperatures i.e. 200°C, 290°C, and up to the final boiling point. From Figure 4, it can be observed that HGPO gave maximum recovery which is around 43% and recovery of LGPO is 19.1% by volume.

From Table 1, it can be observed that crude oil and HGPO have low density than that of diesel i.e. 801 kg/m^3, and the blending of HGPO and LGPO with diesel decreases the density of blends. Lower density favors fuel atomization as well as in proper mixing of air/fuel ratio which affects the energy content of the fuel dose.

Table 1: Density measurement results of samples

Sample	Test Method	Density (kg/m^3)
Crude plastic oil	IS 1448[P16]: 1990 Rev 3rd	801
HGPO	IS 1448[P16]: 1990 Rev 3rd	801
Market Diesel	IS 1448[P16]: 1990 Rev 3rd	828.5
10BHGPO	IS 1448[P16]: 1990 Rev 3rd	826.4
15BHGPO	IS 1448[P16]: 1990 Rev 3rd	824.8
20BHGPO	IS 1448[P16]: 1990 Rev 3rd	823.4
5BLGPO	IS 1448[P16]: 1990 Rev 3rd	827
10BlGPO	IS 1448[P16]: 1990 Rev 3rd	827.1

As per the IS 1460-2017, the maximum distillation recovery of 95% (V/V) of the tested sample should come to the temperature of 360°C [19]. Crude oil on fractional distillation gave both high and low-grade plastic oil. From Table 2, it can be observed that 10BHGPO, 15BHGPO, and 20BHGPO contain lower hydrocarbon as the IBP of these samples are 130.0 °C, 132.00 °C, 130.0 °C, 127.0 °C and 125.0 °C respectively. Recovery of these blends of HGPO and LGPO are above 95%.

From Figures 5, 6 and 7, it can be observed that all the blends of HGPO and low-grade plastic oil follow

Table 2: Distillation result of samples as per ASTM D86

Sample	10% (V/V) recovery Temperature (°C)	50% (V/V) recovery Temperature (°C)	90% (V/V) recovery Temperature (°C)	Recovery (%)	IBP (°C)	FBP (°C)
Diesel	170.30	248.48	311.60	98.5	140.00	336.00
Crude oil	136.70	237.34	312.25	98.00	88.20	322.40
HGPO	195.59	244.98	299.78	98.5	156.00	322.00
10BHGPO	166.78	248.39	316.07	98	130.00	338.00
15BHGPO	167.71	250.74	318.89	98	132.00	340.00
20BHGPO	167.86	246.30	318.78	98.5	130.00	340.00
5BLGPO	172.61	247.56	311.32	98	127.00	336.00
10BLGPO	173.02	256.00	312.79	97	125.00	333.00

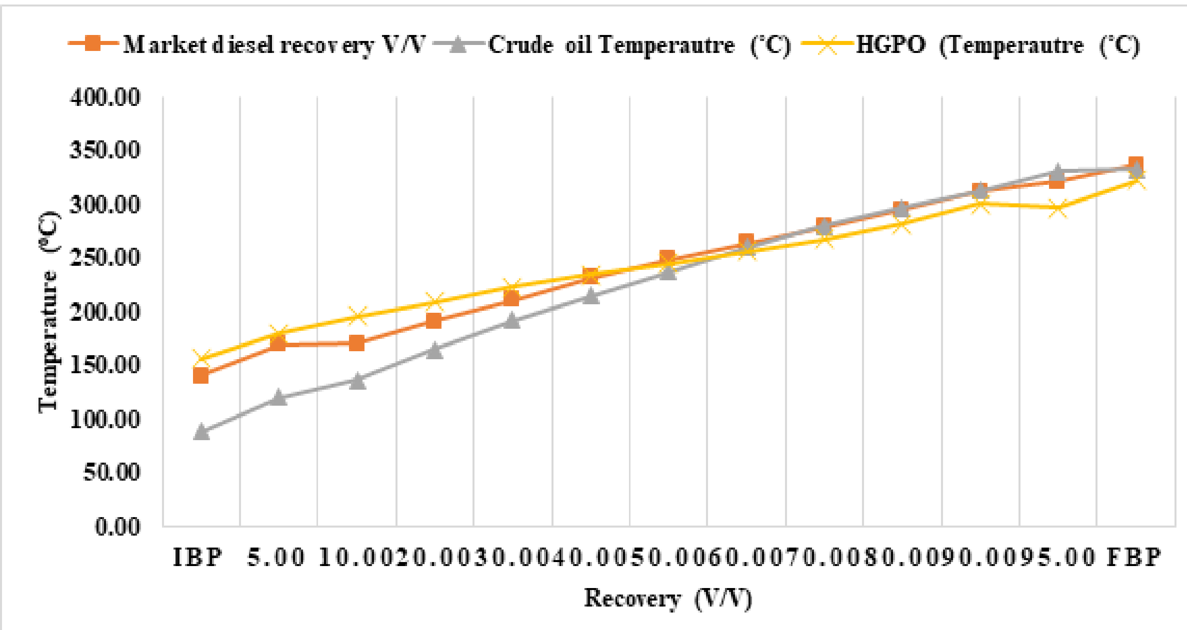

Figure 5: ASTM D976 distillation curve of Diesel, crude plastic oil and HGPO

a similar distillation pattern as that of diesel. There is only a marginal difference in the recovery temperature of these blends. Crude plastic oil contains lower hydrocarbon, the recovery temperature before 60% recovery (V/V) is lower than that of diesel. With HGPO, distillation recovery temperature before 62% recovery (V/V) is higher than that of diesel. This is because HGPO is the distilled plastic oil obtained from crude oil from the temperature range of 200°C to 290°C.

By calculating the cetane index from the four-variable and two variable equation, it was found that distilled fractions of plastic oil on blending with diesel increases the cetane index of fuel. The calculated values of all blends of plastic oil with diesel and other fractional distillates of plastic oil are shown in Table 3.

Table 3: Calculated Cetane index of plastic oil and its blends with diesel

Sample	Cetane Index	
	ASTM D4737	ASTM D976
Crude plastic oil	56.49	57.40
HGPO	61.49	59.58
Market Diesel	48.63	50.10
10BHGPO	49.36	50.83
15BHGPO	50.55	52.02
20BHGPO	50.16	51.36
5BLGPO	49.14	50.39
10BlGPO	50.89	52.22

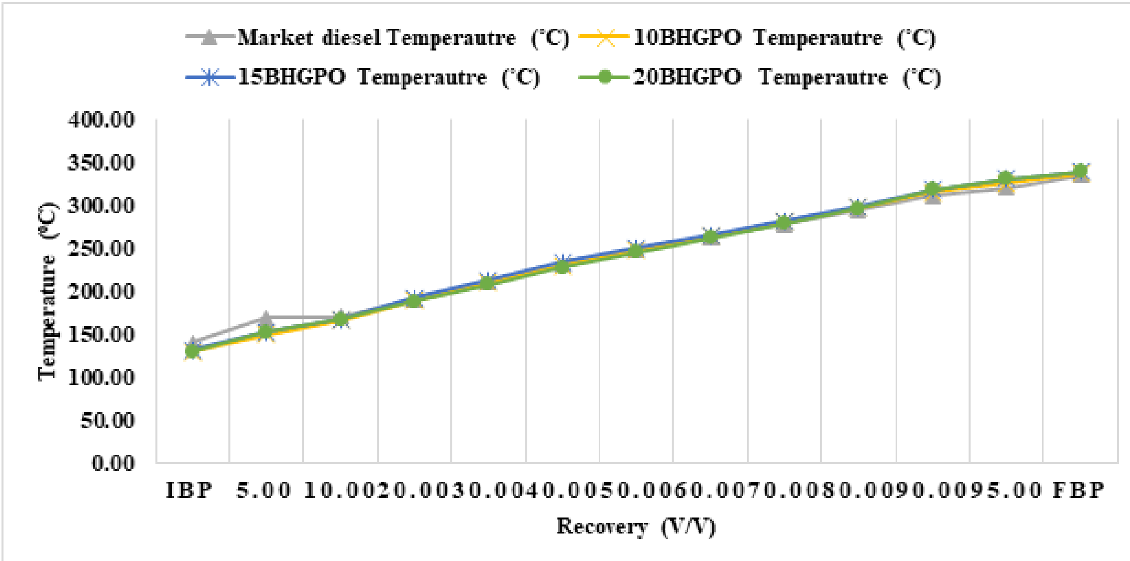

Figure 6: ASTM D86 distillation curve of Diesel, 10BHGPO, 15BHGPO and 20BHGPO

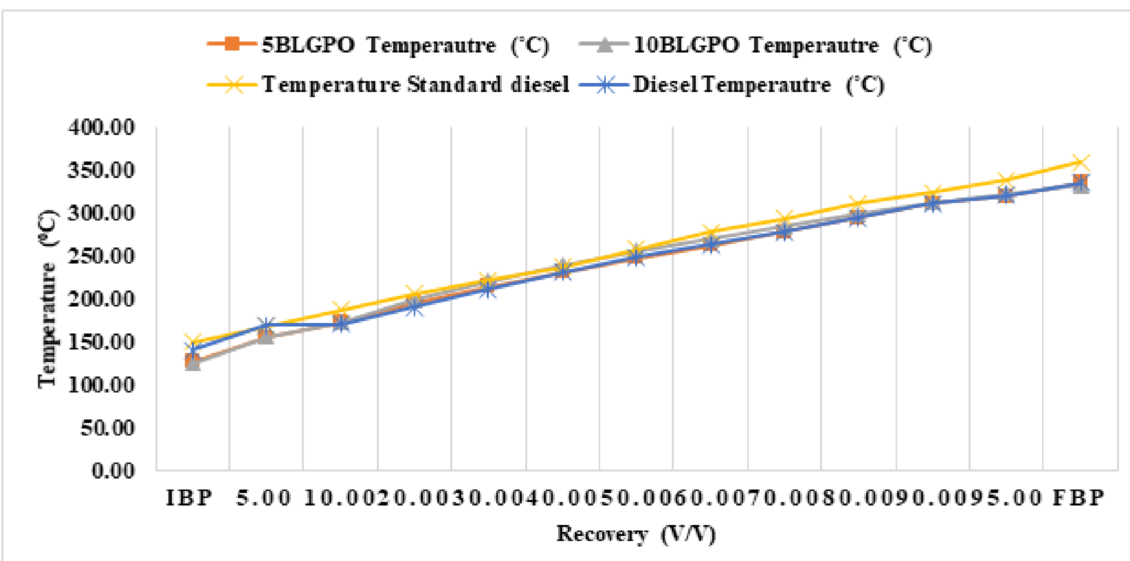

Figure 7: ASTM D86 distillation curve of Diesel, 5BLGPO and 10BLGPO

4. Discussion

Plastic oil has a greater possibility of being used as an alternative fuel in a diesel engine. Recovery of high-grade plastic oil obtained from fractional distillation at a temperature range from 200°C to 290°C has a higher recovery rate. The cetane index of HGPO which was calculated from ASTMD D4737 and ASTM D976 was found higher than the diesel, this may be due to the presence of lower hydrocarbon in HGPO. Blends of HGPO and LGPO show a greater cetane index than diesel. Hence, an increase in the cetane index has a positive impact on engine combustion. As per the IS 1460-2017 standard, plastic oil, HGPO, blends of HGPO and LGPO showed the maximum recovery before 360°C, and the density of all the samples was in the range of diesel. Higher cetane index, density, and recovery from the fractional distillation of the test aided a satisfactory result in the justification of using plastic oil and its blends as an alternative to diesel.

5. Conclusion

The purpose of this study is to investigate the effect of blends of distilled plastic pyrolysis oil with diesel on the cetane index. In addition to the cetane index, the study also focused on distillation temperature and distillation recovery of crude plastic oil. The conclusion of the study on plastic pyrolysis oil and its effect on the cetane index is as follows:

- Plastic pyrolysis oil contains hydrocarbon ranging from lower to higher hydrocarbon. The initial boiling point of crude plastic oil is 88.2°C
- On fractional distillation, both high and low-grade distill plastic to oil is obtained. The recovery of high-grade plastic oil is higher than the low-grade plastic oil.
- Crude Plastic oil and HGPO have a higher cetane index than diesel.
- Blends of high-grade plastic oil with diesel up to 20% by volume and blends of low-grade plastic oil diesel up to 10% by volume show a high cetane index of the fuel which improves the combustion characteristics of the engine.

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