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Recycling of Waste Plastics into Pyrolytic Fuels and Their Use in IC Engines

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Abstract

The energy crisis and environmental destruction are the principal problems in the present day due to the rapid industrialization and growing population. Degradation of solid waste such as plastic bottles, grocery bags, etc. in nature takes many years. Besides, plastic disposing methods like landfill, reusing, and burning can create severe risks to the human health and environment. Therefore, plastic must be kept under control from damaging the environment. One of the most favorable and effective disposing methods is pyrolysis, which is an environmentally friendly and efficient way. Pyrolysis is the thermal degradation of solid wastes at high temperatures to produce pyrolytic oil. The pyrolytic oil produced is converted into pyrolytic fuel very similar to diesel or gasoline by upgrading. The calorific value of the pyrolytic fuel is similar to that of diesel and gasoline. Pyrolytic fuel can be used in internal combustion engines without significant loss in engine performance. Besides, some engine emissions, especially smoke opacity and CO and HC emissions, improve when used with additives or when the engine's operating conditions such as compression ratio and ignition timing are changed. However, NO_x emission is very similar to diesel fuel, too.

Keywords: recycling of waste, waste plastic oil, pyrolytic fuel, alternative fuel, emissions

1. Introduction

Sustainable mobility is described as “the ability to meet society's need to move freely, gain access, communicate, trade and establish relationships without sacrificing other essential human or ecological values, today or in the future” by the World Business Council for Sustainable Development [1]. The main purpose of sustainable mobility approach is to promote mobility solutions that remarkably decrease greenhouse gas emissions, increase energy efficiency, and decrease traffic congestion, creating safer, healthier, and more livable cities and environments [2]. The sustainable mobility approach focuses on the realization of three basic actions as Avoid-Shift-Improve (ASI) framework, which are as follows: (1) Avoid: making less travel (reduce the need for travel), (2) Shift: changing the mode of transport, and (3) Improve: reducing the length of the journey and using more efficient systems in transportation technologies [2, 3]. The third action within the ASI framework focuses on improved efficiency engines with new-generation fuel technology and alternative fuels that reduce the environmental impact of transport. NDC Global

Outlook Report 2019 of the United Nations (UN) states that greenhouse gas emissions should be reduced by 45% over the next decade compared to 2010 and should be net-zero by 2050 [4]. In the transportation sector, it is desirable that the vehicles in transportation consist of electric vehicles and that the electricity consumed is produced from renewable sources in order to reach these targets. However, replacing present internal combustion engine vehicles with zero-emission electric vehicles and generating electricity from renewable sources is so difficult and costly that it will not be possible in a short- and medium-term. As the short- and medium-term activity, it is aimed to reduce greenhouse gas (GHG) emissions below a certain limit by increasing the use of alternative fuels such as biodiesel, bioethanol, and pyrolytic fuels in transportation. These fuels are very important in terms of producing from waste as well as vegetable sources. In addition, the short- and medium-term targets include the development of internal combustion engines with lower fuel consumption and more environmentally friendly.

This chapter will focus on the production of pyrolytic fuel from waste plastics and their use in vehicles. The degradation of plastic materials takes several hundred years and thus, they affect the environment. In landfill areas, waste plastics can release carcinogens and other toxic chemicals that pollute groundwater. In addition, these poisonous chemicals can disrupt soil fertility. Plastic particles floating on the ocean surface are a threat to the marine ecosystem [5]. If waste plastics are used directly as a source of energy and are burned, it creates very harmful emissions to the environment and increases the amount of GHG. In this context, recycling of waste plastic as a fuel through pyrolysis in an inert atmosphere is an environmentally friendly solution. In the last 30 years, there has been a rapid growth in the plastics industry. Worldwide production of synthetic polymers such as polyvinyl chloride (PVC), polypropylene (PP), polyethylene (PE), and polystyrene (PS) has increased more than 100 times in the last 3 years. These plastics are widely used in daily important applications such as household appliances, clothing, food packaging, electronics, and automotive products. While plastics bring great convenience to our lives, the processing of waste plastics is inevitable and must be solved soon [6].

The recycling of plastic wastes is a considerable matter nowadays. Many researchers have investigated the applicability of using waste plastic oil in a diesel engine due to the decrease in fossil resources in the world and the increasing amount of plastic waste. It has been concluded that waste plastic oil has similar properties to diesel fuel and can be used instead of diesel [7, 8]. In this chapter, pyrolysis, one of the alternative fuel production methods, is examined. Types of pyrolysis, types of waste plastics as raw materials, parameters affecting pyrolysis, and products obtained from pyrolysis are presented. In some experimental studies in the literature, the physical and chemical properties of pyrolytic fuels are compared with commercial diesel and gasoline fuels. In the last part, experimental studies on the use of waste plastic pyrolysis oil as fuel in internal combustion engines are given. Waste plastic pyrolysis oil as fuel was evaluated in terms of engine performance, emission, and combustion characteristics.

2. What is pyrolysis?

Pyrolysis is the thermal decomposition of biomass at high temperatures in an inert atmosphere. The process cannot be reversed due to the chemical composition of the material changes. The word pyrolysis is derived from the Greek word pyro “fire” and lysis “separating” [9]. The products formed at the end of pyrolysis include solid coal (char), liquid pyrolysis oil, and gas. Pyrolytic liquid and gas

products can be used for power generation in engines and turbines. Therefore, the pyrolysis of biomass is a promising method for alternative energy sources. This method takes place at high temperatures. The critical temperature ranges for obtaining pyrolysis products is between 350 and 500°C. The process can use self-produced pyrolytic oil or gas to reach such high temperatures [10]. In this respect, the process can be performed by consuming less energy from the outside. During the pyrolysis process, the chemical bonds of the biomass are thermally degraded in an oxygen-free environment and at high temperatures.

Advantages of pyrolysis over other methods are as follows: the amount of harmful wastes released to the environment is low, the end product formation is economical, and it reduces air pollution and supports itself in terms of energy use. Primary products obtained in the pyrolysis process can be used directly or can be converted to high-quality fuel or other chemical products by applying chemical processes. This method is often preferred for the conversion of solid biomass waste, which is difficult to use and cost-effective, into liquid products. The production, transportation, and storage costs of these liquid products are low and their energy density is high. Besides, in the elemental composition of liquid products, there are complex structures of biomass-like and oxidized hydrocarbons.

2.1 Type of pyrolysis

Pyrolysis is divided into three basic groups: slow, flash (intermediate), and fast according to the time and temperature during the process. According to the pyrolysis types given in **Table 1**, the liquid products obtained, especially from the fast pyrolysis processes can be used as internal combustion engine fuel [11].

Slow pyrolysis is slowly heating of organic biomass in the absence of oxygen at nearly 500°C. Instead of combusting, the volatiles from the organic material vaporize partially, and a product called charcoal remains, consisting of a large proportion (approximately 80%) of carbon. Slow pyrolysis is also named carbonization. In the slow pyrolysis, the main product is solid charcoal [12].

Fast pyrolysis is rapidly heating of organic biomass often in the range between 425 and 500°C in the absence of air. Organic vapors, char, and gas are produced under these conditions. In later stages of the process, the vapors are condensed to pyrolytic oil. Commonly, 60–75 wt.% of the feedstock is converted into oil [12].

Flash pyrolysis is a thermal-cracking process at a very high heating rate with a very short vapor residence time with high pyrolysis temperatures around 450 and 1000°C. The main objective of this process is to minimize secondary cracking. Thus, the liquid yields are maximized and can go up to 75% [13].

2.2 Types of plastics as the raw material

In general, different types of plastics have different compositions. Plastic products are manufactured differently to meet different needs. The different types of plastics and their uses are shown in **Table 2**.

Pyrolysis types	Retention time	Rate of heating	Temperature (°C)	Liquid yield (%)
Slow	5–30 min	Low	300–650	<30
Fast	<2 s	Very high	450–600	50–75
Flash	<1 s	High	450–1000	>75

Table 1.
The operating parameters and product yields for pyrolysis types [13–16].






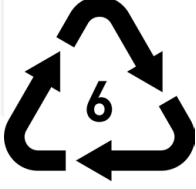

Code	Type of plastics	Common packaging applications
 PETE	Polyethylene terephthalate (PET)	Soft drink, water, and vegetable oil bottles; peanut, butter, and jam jars; salad containers
 HDPE	High-density polyethylene (HDPE)	Milk bottles, yogurt and margarine tubs, waste bags, bowls, cable insulations, liquid detergents, motor oils, shampoos, and perfume containers
 V	Polyvinyl chloride (PVC)	Juice bottles, cling films, soft toys, electrical insulations, roofing materials, pipes and window frame materials
 LDPE	Low-density polyethylene (LDPE)	Frozen food bags; squeezable bottle, e.g., honey, mustard; cling films; flexible container lids
 PP	Polypropylene (PP)	Margarine and yogurt tubes, ketchup bottles, bags for chips and biscuits, disposable cups and plates, medicine bottles, chairs
 PS	Polystyrene (PS)	Egg cartoons; disposable cups, plates, trays, and cutlery; disposable take-away containers; yogurt and margarine containers
 OTHER	Other	Beverage bottles; baby milk bottles

Table 2.
The different types of plastics and their uses.

The chemical composition of the plastic compound includes moisture, fixed carbon, volatile matter, and ash. **Table 3** presents the proximate analysis data of different plastics. The change in biomass composition affects the yields of pyrolysis products. If the amount of volatile matter is high in the plastic content, the liquid yield increases, while the ash content is high, the char yield increases. The ash content is considered low for all plastics, while the volatile matter is very high. These properties mean that plastics may have a high potential to generate a high yield of liquid oil during the pyrolysis process according to the operating conditions [17].

According to ultimate analysis of feedstocks, the carbon (C) ratio by weight in the content of PET is 63.94%. The C ratio of HDPE, PVC, LDPE, PP, and PS is 86.99, 37.24, 85.6, 86.88, and 91.57%, respectively [18]. High carbon content indicates that it will turn into end products with high calorific value.

For plastics, depending on their chemical structure, thermal decomposition begins to occur at different temperatures. For common plastics such as PET, HDPE, LDPE, PP, and PS, the thermal decomposition temperature starts at 350°C, while the thermal decomposition temperature of PVC starts at a temperature lower than 220°C. It is also necessary to adjust the operating temperatures according to the final product preference. For example, if it is desired to produce mostly gas and char, temperatures higher than 500°C are recommended; if it is preferred to produce mostly liquid, it is recommended to apply at temperatures between 300 and 500°C. PET and PVC are rarely investigated by researchers because they produce very low oil yield compared to other types of plastics. Pyrolysis is not recommended for some types of plastics because they contain harmful substances and have low yields such as PVC [19].

Plastic types of polyethylene terephthalate (PET) have become an excellent selection for plastic packaging for a variety of food products, especially drinks such as fruit juice, soft drink bottles, and mineral water cans. In some experimental studies, PET has been used as a raw material in the pyrolysis process with the fixed-bed reactor at 500°C at a heating rate of 10 and 6°C/min. The liquid product yields are 23.1 wt and 39.89 wt%, gas yields are 76.9 wt and 52.13 wt%, and char yields are 0 and 8.98 wt% in these studies [28, 29].

High-density polyethylene (HDPE) is a very strong and economical material. It is not used in products where transparency is important because it has a milk color appearance. Due to its low cost, ease of forming, and break resistance, it has a wide usage area. HDPE is widely used in the producing of detergent bottles,

Type of plastics	Proximate analysis (wt%)			
	Moisture	Fixed carbon	Volatile	Ash
Polyethylene terephthalate (PET)	<0.7	6–14	85–92	<0.1
High-density polyethylene (HDPE)	<0.3	~0	94–99.8	<1.5
Polyvinyl chloride (PVC)	<0.8	5–7	85–94.8	<0.1
Low-density polyethylene (LDPE)	<0.3	~0	99–99.8	<0.4
Polypropylene (PP)	<0.4	<1.2	95–99.6	1–4
Polystyrene (PS)	<0.3	<0.2	99–99.8	<0.5
Other	<0.2	<3	97–99.8	<1

Table 3.
Proximate analysis of plastics [18, 20–27].

milk bottles, toys, oil containers, and more because of its high strength property. In an experimental study, HDPE has been used as a raw material in the pyrolysis process at 350°C using a semibatch reactor. The liquid product yield is 80.88 wt%. In other study at 550°C, the liquid product yield is 79.08 wt% using a semibatch reactor [30, 31].

Polyvinyl chloride (PVC) is available as transparent and semicrystalline material, depending on heat treatment. The most important usage advantage is that it is fully recyclable. It is hard and impact resistant. Thanks to the chlorine (Cl) in the PVC content, it becomes an excellent fire-resistant material and is therefore very suitable for electrical insulation. However, PVC produces hydrochloric acid (HCl) harmful during the pyrolysis [17]. In an experimental study in which pyrolysis of PVC was performed, it is stated that the liquid yield was 12.79 wt%, and hydrogen chloride gas (HCl) yield was found to be 58.2 wt% among all gases (the yield of all gases was 87.7%) [32].

Plastic types of low-density polyethylene (LDPE) have perfect water resistance, so they are widely applied for plastic bags, garbage bags, wrapping foils for packaging, and much more. In some experimental studies in which maximum liquid yield is obtained, LDPE has been used as a raw material in the pyrolysis processes, which are in a fixed-bed reactor at 500°C with a heating rate of 10°C/min, and in a batch reactor at 550°C with a heating rate of 5°C/min. According to these studies, the liquid yields are found at 95 and 93.1%, respectively [33, 34]. In another study, the liquid yield of LDPE was found to be 74.7 wt% using batch reactor at 430°C with a heating rate of 3°C/min [35].

Polypropylene (PP) is a material resistant to chemicals, heat, and extreme fatigue. It is one of the plastics with medium hardness and gloss. PP has a lower density than HDPE but has higher hardness and rigidity that makes it preferable in the plastic industry. In some experimental studies carried out from 300 to 500°C, the liquid yields increased from 69.82 to 82.12% [29, 31, 36, 37].

Polystyrene (PS) is a versatile and multipurpose plastic, very hard, brittle, glossy, and foam-shaped plastic. It is an inexpensive resin with a relatively low melting point. PS offers reasonable durability, strength, and lightness. For this reason, it is used in a variety of sectors such as construction, electronics, medical appliances, food packaging, and toy. In some experimental studies carried out from 425 to 600°C, the liquid yields obtained were between 89.5 and 98.7% [38–40].

2.3 By-products of plastic pyrolysis

The primary products obtained from pyrolysis can be used without treatment. In addition, they can be converted to secondary products after product improvement techniques to improve fuel properties and can be used as a more efficient fuel. In particular, the liquid product obtained from pyrolysis can be converted into a fuel of very similar properties to diesel or gasoline fuel after secondary processes. Thus, the internal combustion engine becomes available as fuel.

The gaseous product of plastic pyrolysis contains mostly carbon dioxide, carbon monoxide, hydrogen, ethane, methane, ethylene, etc. The pyrolysis product gases may provide heat for the pyrolysis reactor, which is part of the system, or may be used for the generation of heat and electricity in a gas turbine combined cycle system.

The solid product that has a high surface area and large pores and that is released as a result of the pyrolysis process applied to biomass can be used as activated carbon. In other words, the content of char is composed of

condensed organic residues and the inorganic phases, with an average high heating value of 28.5–29 MJ/kg [41].

2.4 Operating parameters of pyrolysis

In pyrolysis, the feedstock is heated to a certain temperature at a given heating rate without oxygen and held there for a certain time. During pyrolysis, large hydrocarbon molecules are broken down into relatively smaller ones by reactions such as depolymerization, dehydration, decarbonylation, decarboxylation, deoxygenation, oligomerization, and aromatization [41]. The quantity and proportion of pyrolysis products are influenced by many factors such as biomass composition, pyrolysis temperature, heating rate, and catalyst effect. The fact findings in the 1980s have shown that the yield of pyrolysis oil increases when a biomass feedstock is heated quickly and the produced vapors condense rapidly [12]. These factors and their effects on the pyrolysis process are described below.

2.4.1 Heating rate

The yields of the products obtained in the pyrolysis process vary depending on the heating rate. It is very important to adjust the heating rate to the optimum level as it affects heat transfer. Increasing the heating rate raises the liquid yields and decreases the char yields. The higher the heating rate, the faster the volatiles form, and the lower the heating rate, the longer the residence time for the volatiles. Thus, repolymerization reactions that form char occurs. Higher heating rates minimize char formation. At lower heating rates, the main product is char, which works for a long time (several days). This process is called carbonization.

As the heating rate increases, the conversion degree of the final products and the yield of gases increase, while the yields of oil and char decrease [41]. **Figure 1** shows the typical change in the yields of the final products when there is variation of the heating rate during the pyrolysis process.

Most of the studies in the literature have similar trends like in **Figure 1**; however, the product yields vary according to the raw material used. For example, in a study, the pyrolysis of waste plastic bags in a fixed bed reactor is examined at a pyrolysis temperature of 450°C and the heating rate from 5 to 15°C/min. At heating rates of 5, 10, and 15°C/min., liquid yields are 53.1, 51.3, and 47%, while the yields

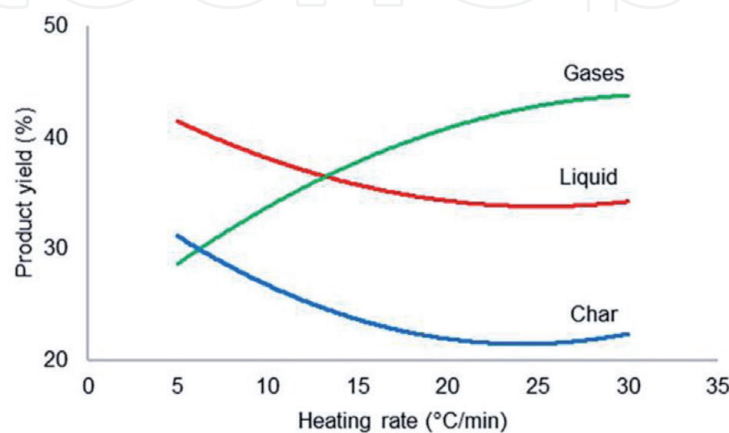


Figure 1.
Yield of the pyrolysis product at various heating rates.

of gases are 32.4, 37.3, and 41%, respectively. Besides, the yields of char are 14.5, 11.4, and 12%, respectively [42].

2.4.2 Temperature

The temperature at which pyrolysis occurs is the most important factor in product distribution. Liquid yield depends on the reaction temperature, biomass type, hot vapor residence time, and catalyst use. It is important to note that the maximum efficiency is not the same as the maximum quality. If the quality of the liquid needs to be optimized, the operating parameters of the process must be carefully defined [16]. According to **Figure 2**, as the temperature increases, the char yield decreases while the yield of the gases increases.

In addition, as the temperature increases up to 500°C, the liquid yield increases. The higher the temperature, the more liquid products turn into gases. After the maximum liquid yield is obtained in the temperature range of 550–550°C, the liquid yield decreases with increasing temperature.

Mostly liquid contains water, oil, and wax. Oil in liquid can be converted into fuel via chemical processes by considering the physical and chemical properties of the fuel. In this case, the oil yield may be slightly lower than the initial liquid yield. In the literature, the changes in temperature of pyrolysis products show similar tendencies. In a study by Pütün [43], bio-oil yields of 41, 46, and 43% were obtained at temperatures 400, 550, and 700°C, respectively.

The yield of the product obtained from the pyrolysis of the plastic mixture in another study, according to the variation of temperature, is shown in **Table 4** [44].

It is clear that the gas percentage increases as the temperature increases. The yield of the char decreases with increasing temperature. It is stated that it supports more gas formation as molecules break down under high temperature and heating rate conditions. In addition, they form much smaller organic molecules under these conditions. When a higher amount of energy is available at a higher temperature, there is a tendency for an increasing number of secondary reactions. The amount of oil and wax decreases with an increase in temperature. At low temperatures, the conversion reactions of solid products to pyrolytic oil decrease and waxy structures increase due to incomplete pyrolysis. Cahyono and Fenti [42] conducted an experimental study using plastic wastes in a reactor at the heating rate of 15°C/min with pyrolysis temperature between 250 and 450°C. **Table 5** shows the yield of the pyrolysis products obtained in the study. Accordingly, the amount of wax decreases with increasing temperature, while the amount of oil and gases increases.

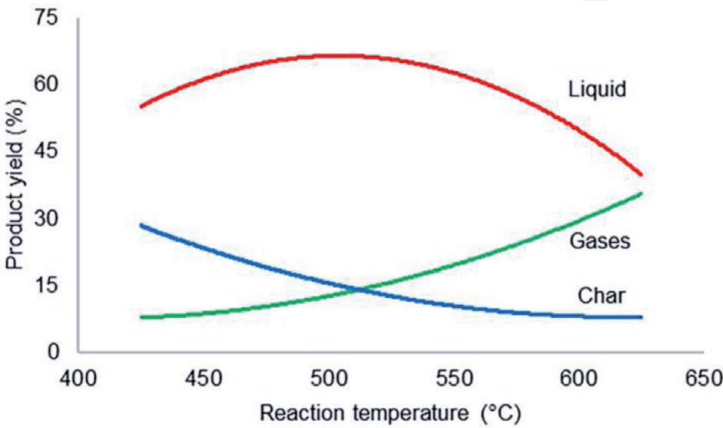


Figure 2.
Yield of the pyrolysis product at various reaction temperatures.

Product (%)	Temperature (°C)				
	500	550	600	650	700
Gas	9.79	24.52	43.33	88.76	68.81
Wax	17.28	18.56	8.72	0	0
Oil	37.79	38.55	34.44	20.49	18.44
Char	2.82	5.87	7.59	–*	–*

*Unavailable.

Table 4.
The product yields from the pyrolysis of the plastic mixture with change in temperature.

Product (%)	Temperature (°C)		
	250	350	450
Gas	5	35	41
Wax	52	27	2
Oil	8	15	45
Char	35	23	12

Table 5.
The product yields from the pyrolysis of the plastic with change in low temperature [42].

When the temperature reaches a higher degree, the initially formed liquid products are transformed into gas via secondary reactions. The main part of the product is solid at low temperatures, while the main product is gas at high temperatures [44].

2.4.3 Particle size

In the literature, it is stated that particle size is significantly effective in the generation of pyrolysis products, especially coal and oil. In general, as the particle size increases, the core temperature of the particle is lower than that of the surface. This results in higher temperature gradients within the particle. Therefore, it takes a long time to complete the pyrolysis process. If fast or flash pyrolysis is to be carried out, it is necessary to divide the biomass into small particles. As a result, char yield increases with increasing particle size and oil and gas yield increases with decreasing particle size. In addition, small biomass particle sizes are needed to achieve high biomass heating rates [16]. Most of the studies in the literature have similar trends like in **Figure 3** for particle size in the pyrolysis process. The yield of the products may vary depending on the raw material.

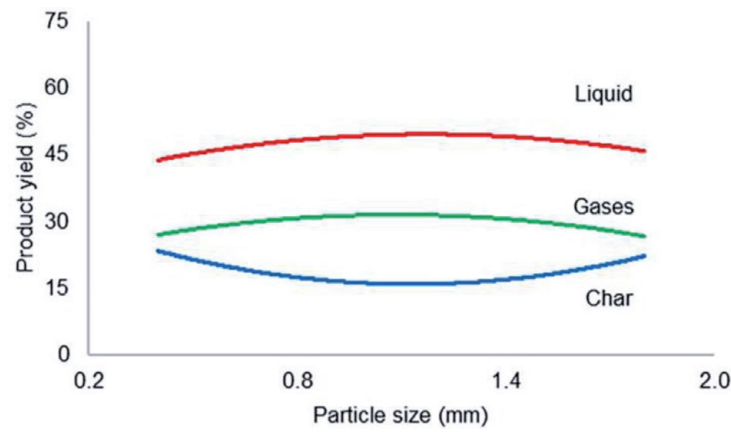


Figure 3.
Yield of the pyrolysis product at various particle sizes.

In the literature, the experimental studies show that particle size does not cause a significant change in char, oil, and gas yield. Ertas and Alma [45] compared the yields of pyrolysis products according to different particle sizes such as $1.60 > P_s > 0.850$, $0.850 > P_s > 0.420$, and $0.420 > P_s > 0.250$ mm in their experimental study (P_s : particle size). It was carried out in a fixed-bed reactor at the optimum temperature (500°C). Nonetheless, the optimum particle size for maximum bio-oil yield is shown as the medium particle size. The gas yield for the large particle size was measured slightly higher than the other dimensions, and the char yield for the small particle size was measured slightly lower than the other dimensions.

2.4.4 Residence time

Volatile residence time is a significant factor to affect yields of liquid and gaseous products in a biomass. A longer residence time allows the formation of secondary reactions such as thermal cracking, repolymerization, and recondensation, thereby reducing liquid yield [46]. Higher temperatures and longer volatile residence times enhance biomass conversion to gas. Mild temperatures and short volatile residence time are optimum for liquids [12].

2.4.5 Catalyst effect

The catalyst is used to accelerate the chemical reaction. In the process using the catalyst, the activation energy of the process is reduced and thus the reaction rate is increased. This case reduces the optimum temperature required for the process. The most important parameter that prevents the application of the pyrolysis process is high energy consumption. So, the use of a catalyst can help save energy [17]. The reaction time is shortened by using a catalyst in the pyrolysis of plastic biomass. Panda carried out pyrolysis of three different types of plastics (PP, LDPE, and HDPE) by changing catalyst to biomass ratios of 1:0, 1:20, 1:10, and 1:3 at 500°C reaction temperature. The reaction time has been shorter when the ratio of catalyst to biomass has increased in his study. When HDPE has been used as biomass, the reaction time without catalyst has been 83 minutes, while the reaction time has been reduced to 64 minutes with 33.3% (1:3) catalyst. The specific gravity of the pyrolysis oil measured 0.853 g/cm^3 when using %5 (1:20) catalyst in the pyrolysis process while it measured 0.789 g/cm^3 when using %5 (1:20) catalyst [47]. By using different catalysts and determining the optimum catalyst/biomass ratio, more chemically homogeneous and different ratios of pyrolysis products can be obtained. In recent years, various biomass-derived waste materials have been investigated using various catalysts to understand the effects of the catalyst in the pyrolysis process.

2.5 Catalysts

The catalysts are widely used in industries and research to optimize product distribution. In the reactor, the use of catalysts for pyrolysis of polyolefins increases the selectivity of volatile products by changing the product distribution [17]. Especially catalysts are of great interest in the production of automotive fuels such as gasoline and diesel [48]. The catalyst has been used by many researchers for product upgrades to improve the hydrocarbon distribution to obtain the pyrolysis liquid, which has similar properties to conventional fuel such as gasoline and diesel.

There are two structures of catalysts, which include only one phase (homogeneous) and more than one phase (heterogeneous). The most common type of catalyst used is heterogeneous because the solid catalyst is easily separated from the liquid product mixture. Heterogeneous catalysts are preferred because the catalysts

can be reused [17]. Thus, the use of highly costly catalysts becomes more economical. Zeolite, silica (SiO_2), calcium oxide (CaO), and alumina (Al_2O_3) are the most commonly used catalysts in the pyrolysis process because of reducing the temperature required to complete the reaction and enhance the reaction rate [49].

3. Characteristics of pyrolytic fuel

Plastic waste is now one of the significant elements of municipal solid waste (MSW). It is a mixture of different plastic products, largely made from high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET), and polyvinyl chloride (PVC). PS and PE are the most common types of plastics in municipal waste [50]. Plastics are nonbiodegradable polymers mostly containing carbon, hydrogen and few other elements [6]. The elemental analysis of pyrolytic oil and other fuels is given in **Table 6**.

After the oils produced in pyrolysis were removed from visible precipitates, the appearance of the liquid fuel obtained from HDPE is light yellowish. The liquid fuel obtained from PS is seen as dark yellow, while the liquid fuel obtained from PP is seen as deep brown [53].

Density, kinematic viscosity, thermal value, flash point, cetane number, octane number, and cold filter plugging point are among the most important physical and chemical properties of fuels used in internal combustion engines. These characteristics affect the usage decision of fuel in internal combustion engines. Some of the physical and chemical properties of pyrolytic fuels produced from different types of plastics are presented in **Table 7**.

Density is an important fuel feature that affects fuel consumption and sprays characteristics. The densities of liquid fuels produced from HDPE, PS, and PP have been given 0.796, 0.894, and 0.786 g/cm^3 , respectively [53].

Kinematic viscosity adjusts the spray pattern and atomization of injected fuel in a combustion chamber [54]. Generally, the fuels with high viscosity are not preferred for internal combustion engines because they lead to poor engine performance. The high viscosity makes it difficult to transport the fuel to the fuel supply system. This condition limits the use of high viscosity fuels in winter. In addition, the use of low viscosity fuels can cause serious pump and injector leakage. This may lead to a drop in fuel distribution and a reduction in the engine power output. Low kinematic viscosity demonstrates that pyrolytic oil contains high amounts of gasoline and low amounts of heavy oil. The kinematic viscosities of pyrolytic liquid fuels produced from HDPE, PS, and PP were given as 2373, 1461, and 2115 mm^2/s , respectively [53].

Raw material of fuel	Elemental analysis (wt%)					High calorific value (MJ/kg)
	Carbon	Hydrogen	Nitrogen	Sulfur	Others	
HDPE	85.49	14.23	—	0.28	—	43.92
LDPE	85.44	14.31	—	0.25	—	43.28
PP	83.80	13.85	—	0.33	2.02	38.10
PS	91.48	7.41	—	0.19	0.92	38.53
PVC	39.17	4.96	—	0.58	55.29	22.45
MPW*	84.30	12.25	<0.1	0.38	3.00	39.72
Diesel [51]	85.60	14.10	0.30	—	—	45.19

*Municipal plastic wastes.

Table 6.
Characteristics of pyrolytic fuels from different plastic types [51, 52].

Properties	PET	HDPE	PVC	LDPE	PP	PS	Gasoline	Diesel
Calorific value (MJ/kg)	28.2	40.5	21.1	39.5	40.8	43.0	42.5	43
Viscosity (mm ² /s)	n.a	5.08 ^a	6.36 ^b	5.56 ^c	4.09 ^a	1.4 ^d	1.17	1.9–4.1
Density @ 15°C (g/cm ³)	0.90	0.89	0.84	0.78	0.86	0.85	0.78	0.81
Pour point (°C)	n.a	−5	n.a	n.a	−9	−67	—	6
Flash point (°C)	n.a	48	40	41	30	26.1	42	51
Octane number MON (min)	n.a	85.3	n.a	n.a	87.6	n.a	81–85	—
Octane number RON (min)	n.a	95.3	n.a	n.a	97.8	90–98	91.95	—
Diesel index	n.a	31.05	n.a	n.a	34.35	n.a	—	40
<i>n.a.</i> not available. ^a at 40°C. ^b at 30°C. ^c at 25°C. ^d at 50°C.								

Table 7.
Fuel characteristics of plastic pyrolytic fuel [19].

Pour point is known as the temperature at which the fluid stops to flow. Generally, the increase in viscosity may cause the fluid to lose its flow feature. If liquid fuel has a lower pour point, it has lesser paraffin content but greater aromatic content [17].

In order to prevent fire hazard during storage, one of the important features of the fuel is the flashpoint. The flashpoint of the liquid is defined as the lowest temperature at which the liquid-vapor mixed with the air ignites when an external flame is applied [55]. The flashpoint of HDPE, PVC, and LDPE pyrolysis oil was very close to commercial gasoline.

It is desirable to have a high cetane index as an indicator of the excellent combustion properties of the liquid product. The high cetane index is associated with the presence of α -olefins and linear paraffin [31]. Distillation is the process by which a liquid mixture is separated into its components by heating and condensing to a certain temperature. In this process, the initial boiling point (IBP, °C) is determined by the temperature at which the first distillation drops. The final boiling point (FBP, °C) is the temperature at which all the oil sample in the distillation chamber evaporates. The distillation temperatures of 10, 50, 90, and 95% volumes in the recovered volume are recorded as well as the determination of IBP and FBP. Using these temperature data, estimating the calculated cetane index (CCI) of the fuel can be calculated by a four-variable equation according to ASTM D4737 [5]. The boiling temperatures of the different fuels and the mass distribution of the distilled fuels are shown in **Figure 4**.

Pyrolytic oil is compared with diesel, kerosene, and gasoline. It is clear from this figure that pyrolytic oil consists of compounds in the gasoline range, as well as compounds in the range of kerosene and diesel. The starting and ending temperatures of boiling and the thermal values of the conventional fuels are given in **Table 8**. Considering that the liquid at boiling point higher than 150°C is kerosene or diesel, the pyrolytic oil contains approximately 35% gasoline according to **Figure 4**. The rest consists of kerosene and diesel fuel.

The calorific values of some plastics, such as HDPE, PP, and LDPE, have more than 40 MJ/kg [17]. These values may be considered sufficient to be used as fuel. In some studies, the calorific values of HDPE and PP have been reported to be more than 45 MJ/kg, which indicates that these fuels are produced very close to gasoline and diesel fuel [31]. In general, PET and PVC have the lowest calorific value below

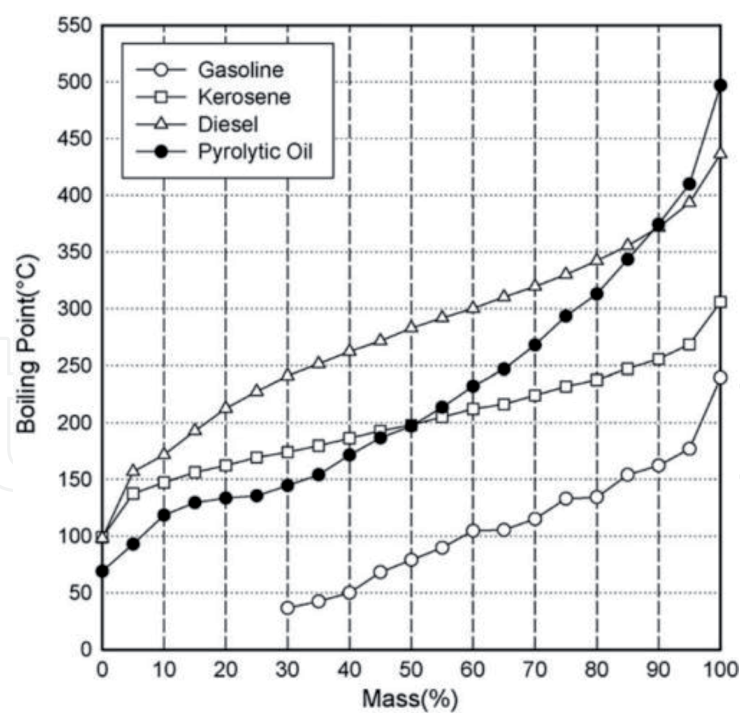


Figure 4.
Distributions of boiling point range of fuel samples [56].

Fuel	Boiling point (°C)	Calorific value (MJ/kg)
Gasoline	40–200	43.4–46.5
Kerosene	150–300	43.0–46.2
Diesel	150–390	42.8–45.8

Table 8.
Boiling point and calorific value of conventional fuels [57].

30 MJ/kg due to the presence of benzoic acid in PVC and chlorine compound in PVC, which reduced fuel quality [17].

The release of hydrochloric acid and chlorine compound during the PVC pyrolysis indicated that the liquid oil was not suitable to be used as a fuel since it depreciated between the fuel quality [17].

The liquid oil that is produced through plastic wastes via pyrolysis may contain certain substances such as sulfur, chlorine, solid residue, moisture, and acids. The presence of these substances not only reduces the quality of the liquid oil but also limits its commercial use. Therefore, liquid oil requires posttreatment, including upgrading to removal of char particles and acids, and neutralization to improve liquid oil with stable pH, and low corrosivity. There are two ways to make the pyrolysis liquid commercially available. One of them is to blend pyrolysis liquid with diesel fuel to provide certain fuel properties. The other is refining. Liquid pyrolysis oil can be used in modified diesel engines after upgrading to fuel and removing from impurities.

4. Use of plastic pyrolysis oil as fuel in the IC engines

Mani et al. [7] have obtained fuel by feeding waste plastics into a reactor along with 1 wt.% catalyst and 10 wt.% coal at a temperature of 300–400°C for about 3–4 hours at atmospheric pressure. In this process, they produced 75% liquid and tested using it in the engine. The engine tests were conducted on a single-cylinder, four-stroke,

air-cooled diesel engine at a constant speed of 1500 rpm under 4.4 kW load. The physical and chemical properties of test fuels are as follows: the density, viscosity, high heat value (HHV), and cetane number of the diesel fuel are 0.840 g/cm^3 , $2.0 \text{ mm}^2/\text{s}$, 46.5 MJ/kg , and 55, respectively, while those of waste plastic oil are 0.836 g/cm^3 , $2.52 \text{ mm}^2/\text{s}$, 44.34 MJ/kg , and 51, respectively. It is stated that the ignition delay in the test using waste plastic oil was considerably longer than that of the test using diesel. The longer ignition delay in the waste plastic oil caused the cylinder peak pressure for diesel is 67 bar at rated power and 71 bar in the case of waste plastic oil. During the premixed combustion phase, the longer ignition delay resulted in a higher heat release rate usage of waste plastic oil. NO_x emission for waste plastic oil increased by approximately 25% compared to diesel. The amount of NO_x increased when the temperature inside the cylinder rose. Furthermore, the residence time of the fuel in the reactions affected NO_x formation [31]. It is expressed that the high heat release rate increased the exhaust gas temperature and triggered NO_x formation. In the case of waste plastic oil usage, HC emissions increased by approximately 15% compared to diesel. Besides, it is stated that the CO emission of waste plastic oil was higher than that of diesel. The CO_2 emission in the waste plastic oil was generally lower than the CO_2 emission in the diesel, except under full load conditions. The smoke of waste plastic oil decreased by approximately 40% according to that of diesel at rated power. In terms of engine performance, the thermal efficiency was calculated as 28.2% at rated power for diesel and 27.4% for the waste plastic oil.

In another study, Mani et al. [58] collected plastic HDPE grocery bags from local retailers and produced a fuel using a pyrolysis batch reactor. After that, they mixed waste plastic oil and diesel fuel in certain proportions and tested in a diesel engine. The mixture of 10% waste plastic oil and 90% diesel fuel was named WPO10. Similarly, WPO30, WPO50, and WPO70 mixtures were prepared. The WPO30 fuel blend produced results very close to the engine test results obtained from diesel fuel. In this study, it is stated that it can be used by mixing diesel and waste plastic oil.

Gungor et al. [59] produced the waste polyethylene fuels via the pyrolysis process in their study. Thermal cracking experiments were realized for 1 hour over 400°C . Waste polyethylene fuel obtained from experiment is named WPE. The physical and chemical properties of test fuels are as follows: the density, viscosity, calorific value, and cetane number of the diesel fuel are 0.833 g/cm^3 , $2.52 \text{ mm}^2/\text{s}$, 45.1 MJ/kg , and 54.6, respectively, while those of WPE are 0.788 g/cm^3 , $2.33 \text{ mm}^2/\text{s}$, 45.5 MJ/kg , and 43.7, respectively. This fuel was mixed with conventional diesel fuel with volumetric ratios of 5, 10, 15, 20, and 100%. In the experiments, a diesel engine with four-stroke, four cylinders at 1800 rpm was used. The engine performance and exhaust emissions of the pyrolytic fuels were determined and they were compared with those of diesel. Power output of the engine in WPE5 blend increased maximum by 1.63% compared with diesel. Torque output of the engine in WPE5 usage decreased by 2.73% compared to diesel, especially at higher engine speeds. While CO emission decreased by 20.63% when WPE5 blend was used and CO_2 emission increased by 3.34% when WPE5 blend was used. Besides that, NO_x emission increased by 9.17% with WPE5 usage compared to diesel.

Guntur et al. [60] investigated the performance and emission characteristics of a diesel engine with single-cylinder, constant speed, and direct injection using waste plastic pyrolysis oil blends as an alternative fuel. The waste plastic pyrolysis oil (WPPO) was blended with diesel fuel with volumetric ratios of 50 and 70%. Results indicated that the brake thermal efficiency was higher compared to diesel at part load condition. HC (except for 100% load), CO, and CO_2 emissions of WPPO50 and WPPO70 fuels were found higher than diesel fuel at all loads.

Kaimal and Vijayabalan [61] collected waste plastics from the municipal disposal site and separated them into small chips (0.5–1 cm²). They were mixed with 10 wt% coal and 1 wt% silica catalyst to perform pyrolysis. At the end of the pyrolysis process, the yield of plastic oil is 80% by input weight. The yield of solid coke residue is 15% by weight and the yield of gaseous fractions (a mixture of propylene, isobutane, ethane, and methane) are 5% by weight. The experiment was conducted on direct injection, single-cylinder, water-cooled diesel engine at 1500 rpm generating 3.7 kW. Tests were conducted for diesel fuel, plastic oil mixtures (PO25, PO50, and PO75), and neat plastic oil (PO100). Due to the higher oxygen content and the higher calorific value of the plastic oil, the maximum heat release is significantly increased for plastic oil and its blends. It was reported that the highest thermal efficiency was 31.46% for diesel at full load. In addition, it is stated that the brake thermal efficiency of PO25, PO50, and PO75 mixtures are 30.07, 29.17, and 28.26%, respectively.

Kalargaris et al. [62] conducted an experimental study by producing via a fast pyrolysis process using a feedstock consisting of different types of plastic. Feedstock composition consists of styrene-butadiene (47%), polyester (26%), clay (12%), ethylene-vinyl acetate (7%), rosin (6%), polyethylene (1%), and polypropylene (1%). Density, kinematic viscosity, flashpoint, and LHV of produced plastic pyrolysis oil (PPO) are 0.9813 g/cm³, 1.918 mm²/s, 13°C, and 38.3 MJ/kg, respectively. The properties of diesel control fuel are 0.8398 g/cm³, 2.62 mm²/s, 59.5°C, and 42.9 MJ/kg, respectively. PPO was tested in a four-cylinder, turbocharged, direct injection, water-cooled diesel engine. The experiments were carried out at the rated engine speed of 1500 rpm and at different engine loads from 25–100%. Five blending ratios of PPO and diesel, namely 25, 50, 75, 90, and 100% (v/v%), were tested at each load. They reported that cylinder peak pressures enhanced with increasing PPO content in the blend at full load. The lower viscosity of the PPO improves the atomization, thus resulting in increased HRR values of PPO blends. In addition, the oxygen content (3.3 wt.%) in the PPO may contribute to the high HRR of PPO blends. In the study, it was stated that BSFC increased and BTE decreased with an increasing amount of PPO in the blend. In addition, BSFC decreased with increasing engine load and BTE increased. A similar trend was observed in all mixtures. Increased percentage of PPO in the blend also increased EGT. NO_x emission increased both with increasing engine load and increasing PPO ratio in the blend. The CO emission of the PPO blends was measured very close to that of the diesel at high engine loads, while the CO emission was very high in blends with a high PPO ratio at low loads. UHC and CO₂ emissions are higher in PPO blends than in diesel.

Kumar et al. [63] in their study evaluated performance and emission analysis of blends of waste plastic oil obtained by catalytic pyrolysis of waste high-density polyethylene with diesel in a CI engine with varying loads. The physical and chemical properties of test fuels are as follows: the density, viscosity, and gross calorific value of the diesel as control fuel are 0.83 g/cm³, 2.58 mm²/s, and 43.8 MJ/kg, respectively, while those of waste plastic oil are 0.79 g/cm³, 2.1 mm²/s, and 40.17 MJ/kg, respectively. The experimental results show that the brake thermal efficiencies at all load conditions are lower as compared to those of diesel fuel and exhaust gas temperature increases with increase in engine load. The BSFC increases with increase in WPO blend ratio and decreases with increase in engine load. Mechanical efficiency increases with increasing brake power for all fuel blends. The NO_x emission and CO emission increase with increase in the percentage of waste plastic oil in blends, and NO_x emission decreases while CO emission increases with increase in engine load. The unburned hydrocarbon emission decreases with increase in the engine load and increases with an increase in the percentage of waste plastic oil in blends. The CO₂ emission for the blends is lower than diesel for almost all loads and all blends.

In a study, Mani and Nagarajan [64] showed that the emissions can be reduced by making some modifications in the engine. In the tests carried out with waste plastic oil, the conditions where the standard injection timing of the engine is 23° bTDC and the delayed injection timing is 14° bTDC were compared. After this modification, if the waste plastic oil is used in the engine, it can be possible to obtain results that are equivalent to the results of diesel usage at standard injection timing [7, 64]. When waste plastic oil was used in engine tests with standard injection timing, the ignition delay was longer than that of engine tests with delayed injection timing. A longer ignition delay caused the cylinder peak pressure to rise. It is stated that the cylinder peak pressure is low for the delayed injection timing. The cylinder peak pressure in the engine test with delayed injection time decreased by 6% compared to the engine test with standard injection time at full load. The heat release rate in the delayed injection time decreased by 6% compared to standard injection time at full load. At full load, the brake specific fuel consumption in standard injection timing diminished due to the long ignition delay. The reduction of the brake specific fuel consumption in delayed injection timing led to its high thermal efficiency. The thermal efficiency is 28.2% for standard injection timing, while it is 32.25% for the retarded injection timing. The high thermal efficiency indicates less heat loss. The exhaust gas temperature for the delayed injection time is lower than that of the other. This is explained by the fact that there is less heat loss in the study. The emission of NO_x for retarded injection timing decreased at all loads by approximately 11% to standard injection timing. Because lower peak pressures result in lower peak temperatures, it is seen that retarded injection timing of the engine diminishes the unburned HC emissions. The unburned HC emissions in the engine test with delayed injection time dramatically reduced compared to the engine test with standard injection time. It is explained that the CO emissions were lower for delayed injection timing by 25% compared to standard injection timing in an engine fueled with waste plastic oil. However, the smoke for the delayed injection timing increased compared to the standard injection timing.

Damodharan et al. [5] produced fuel from waste plastics via pyrolysis and tested it at 5.2 kW rated power and 1500 rpm constant speed in a diesel engine with single-cylinder, water-cooled, and direct injection. The effects of injection timing and EGR ratio of the engine were investigated in tests using waste plastic oil (WPO). Properties of test fuels include the following: for diesel, the lower heat value (LHV) is 41.82 MJ/kg, the viscosity is $3.8 \text{ mm}^2/\text{s}$, the density is 0.838 g/cm^3 , the cetane number is 54, and the flashpoint is 70°C , while for the WPO, they are 40.35 MJ/kg, $2.16 \text{ mm}^2/\text{s}$, 0.813 g/cm^3 , 51, and 38°C , respectively. It is stated that the standard injection timing of the engine is 23° bTDC and tests are performed at 25° , 23° , and 21° bTDC injection timing. In addition, 10, 20, and 30% EGR rate was used in the tests using neat WPO and compared with the results of diesel at standard injection timing. The peak in-cylinder pressures and heat release rates (HRRs) were reported to be dropping gradually as the injection timing was delayed from 25° bTDC to 21° bTDC. In early injection, waste plastic oil had sufficient time to mix with air and produce a better mixture for combustion. Thus, it resulted in higher pressure and better combustion leading to HRR peaks. In addition, early injection prolongs ignition delay and improves combustion. In this way, fuel consumption drops. It is seen that the minimum fuel consumption is at 25° bTDC. Brake specific fuel consumption (BSFC) steadily enhanced with rising EGR rates at all injection timings. The trend was similar at all injection timings. Brake thermal efficiency (BTE) diminished with increasing EGR rates at all injection timings. For instance, BTE deteriorated from 34.7 to 28.6%, when the EGR rate was increased from 10–30% at 23° bTDC. The trend was similar to both early and late injection timings. BTE of the engine with WPO used at the early injection timing of 25° bTDC under 10% EGR rate was seen to be better than diesel at standard injection timing without EGR.

by 5.1%. NO_x emissions were lower than diesel usage at standard condition (standard injection timing of 23° bTDC without EGR) when the injection timing delayed at all EGR rates. HC, CO, and smoke decreased with the delay of injection timing. However, these emissions increased with the increase of EGR. HC emission with WPO used at the early injection timing (25° bTDC) under 10% EGR rate was lower than diesel usage at standard condition. However, in other conditions, it was higher than diesel. CO and smoke emissions with WPO used at the early injection timing (25° bTDC) under 10 and 20% EGR rates were lower than diesel usage at standard conditions. As a result, it is expressed that WPO fuel usage at 10% EGR rate in early injection timing increases performance and reduces emissions, instead of diesel usage under standard conditions.

Ramesha et al. [65] carried out pyrolysis using plastic waste as a raw material without oxygen and at a high temperature of about 250–300° C. In addition, they obtained biodiesel from microalgae. They mixed B20 (20% algae oil methyl ester +80% diesel) fuel and waste plastic oil and used it in experiments. The new fuel mixture was named B20AOME10WPO (10% waste plastic oil +90% B20 algae biodiesel). A direct-injection, single-cylinder, four-stroke, and water-cooled diesel engine was used to perform the engine experiments. The motor was run at 1500 rpm and the load was gradually changed between 0 and 100%. Performance, emission, and combustion characteristics were observed and reported. At full load, the BTE was observed to be higher according to diesel control fuel for plastic oil-biodiesel-diesel blend and biodiesel-diesel blend by 15.7 and 12.9%, respectively. At full load, the BTE was observed to be higher according to diesel control fuel for plastic oil-biodiesel-diesel blend and biodiesel-diesel blend by 15.7 and 12.9%, respectively. For plastic-biodiesel-diesel blend, the emission of UBHC and CO decreased when plastic-biodiesel-diesel blend used. And NO_x emission of plastic-biodiesel-diesel blend increased to pure diesel.

Ananthakumar et al. [66] carried out pyrolysis of waste plastics in the absence of atmosphere. The test fuels were prepared with 2.5, 5, and 7.5% by volume of waste plastic oil, 2.5% diethyl ether (DDE), and the remaining by volume of diesel fuel. All blends with DDE additives are named as P2.5, P5, P7.5, and other test fuels are diesel and P100 (100% waste plastic oil). The density, caloric value, flash point, viscosity, and cetane number of the diesel fuel are 0.840 g/cm³, 44.8 MJ/kg, 50°C, 2 mm²/s, and 42, respectively. These properties of P100 are 0.790 g/cm³, 43.34 MJ/kg, 42°C, 2.52 mm²/s, and 51, respectively. These properties of DEE are also 0.714 g/cm³, 33.86 MJ/kg, –40°C, 0.23 mm²/s, and 126, respectively. Experimental study for waste plastic oils and mixtures was made with a variable compression ratio engine. The results of the test for waste plastic oil and its blends were compared with diesel fuel. It has been shown in the study that waste plastic oil can be used as an alternative to diesel at higher compression ratios without any modification to the engine. Mixing waste plastic oil and diesel with additive diethyl ether gave similar results to the diesel. CO₂ emission reduced for WPO and its blends on comparing with diesel. Nevertheless, the CO emission increased. Unburned hydrocarbon and smoke emission were close to diesel in the case of P2.5, P7.5, and P12.5 use. The maximum pressure and rate of heat release for P2.5 and P7.5 were almost similar to those of diesel. Due to the higher rate of heat release and combustion temperature, NO_x emission of WPO and its blends were high. Therefore, waste plastic oil can be blended with diesel and additives like DEE to get comparable results with diesel at higher compression ratios.

5. Conclusion

The rapid increase in plastic production in recent years means that new plastic wastes, which may harm the environment in the coming years, will increase rapidly.

Although plastic products make our lives easier, being insoluble in nature for many years will cause serious environmental problems. The elimination of environmental pollutants with more environmentally friendly solutions is the main issue of sustainable development. In this context, recycling of plastic wastes should be considered in a way that both pollute the environment less and help to consume fewer petroleum resources. At high temperatures and without oxygen, plastics in the municipal solid waste can be recycled using the pyrolysis process and more than 75% of the initial weight can be obtained as pyrolytic oil. The pyrolytic oil can be produced in a very similar composition to diesel or gasoline by some distillation processes. In addition, fuel properties can be improved by some upgrade methods. As a result, a pyrolytic fuel can be produced that can be conveniently used in internal combustion engines. However, when this pyrolytic fuel produced from plastic wastes is used directly in the engine, there is a slight decrease in performance and combustion characteristics. Exhaust emissions are slightly increased compared to standard diesel fuel. In order to overcome these drawbacks, diesel performance additives such as diethyl ether (DDE) may be added to the pyrolytic fuel. Furthermore, engine performance and combustion characteristics can be improved by altering engine operating conditions such as ignition timing and compression ratio. In addition, the exhaust emissions of pyrolytic fuel can be reduced relative to diesel fuel. Consequently, pyrolytic fuels produced from plastic wastes can be used as an engine fuel to pollute the environment less.


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