



The Fuel Production for Diesel Engine from Catalytic Pyrolysis of Plastic Waste

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Abstract

This study compares synthetic and natural catalysts for plastic waste pyrolysis, focusing on ZSM-5 as the synthetic catalyst and dolomite and kaolin as natural alternatives. Investigating polyethylene (PE), polypropylene (PP), and high-density polyethylene (HDPE), the study employed a consistent 500 °C reaction temperature for two hours, utilizing 1 kg of waste and catalyst. Testing the resulting fuel in a single-cylinder diesel engine revealed that PE pyrolysis with kaolin catalyst produced the highest yield at 60.4 wt%. The ZSM-5 synthetic catalyst notably improved fuel calorific value, leading to a 10.0 HP brake horsepower when used in the engine. Conversely, natural catalysts lowered fuel calorific value, causing reduced brake horsepower and increased fuel consumption. However, the kaolin catalyst derived fuel demonstrated effective pollution reduction in engine exhaust due to its benzene group's chemical constituents and suitable oxygen content. The study suggests extending the application of natural catalysts to diverse raw materials for fuel production.

Keywords: Catalytic pyrolysis; Diesel engine; Fuel; Plastic waste.

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1. Introduction

Plastic waste biodegrades naturally very slowly, leading to environmental problems. The researchers then devised a quick way to degrade plastics, such as degradation to produce of gas fuel^[1-3] or liquid fuel.^[4-9] The production of gas fuel was limited for fuel storage because the produced gas must be forwarded to use direct. While liquid fuel production can store produce to transport and use as needed. Production of liquid fuel from plastic waste was a pyrolysis process.

The pyrolysis of plastic waste was setup reaction temperature of 500 °C^[4] and condenses the vapor of pyrolysis rapidly to liquid fuel. The production of liquid fuel from polyethylene bag (PE) and high-density polyethylene (HDPE).^[10] It was found that all plastics gave 50 and 55 wt% differences in liquid fuel content, respectively. The properties of biofuel were analyzed revealing a viscosity of 1.8 cSt, a density of 0.8 kg/m³ and a high heating value of 46 MJ/kg. Meanwhile, the liquid fuel from HDPE had a density of 0.7

kg/m³, a viscosity of 2.3 cSt and a heat value of 42 MJ/kg. When pyrolysis of both plastics with a catalyst, it was found to increase the hydrocarbons C₂-C₁₂ by more than 5 wt% and reduce the viscosity.^[10] The hydrocarbons were different when plastic pyrolysis of polyethylene terephthalate (PET), polypropylene (PP), high density polyethylene (HDPE) with a H-ZSM-5 catalyst.^[11] The plastic pyrolysis of waste electrical and electronic equipment by catalyst.^[12] It was found that the ZSM-5 catalyst can increase a benzene up to 10 wt% and increase the gas hydrocarbons C₂-C₄ by more than 20 vol%. The plastic pyrolysis with the ZSM-5 catalyst increased the calorific value of the liquid fuel by about 7 MJ/kg, and this fuel was more than 10 times more flammable.^[4] This has been shown that the catalytic pyrolysis of plastics with ZSM-5 can improve some liquid fuel properties.

ZSM-5 functions as a catalyst with a high cost due to its synthetic nature. The potential to lower production expenses arises if an economical alternative catalyst can be identified to replace ZSM-5. Research has highlighted the efficacy of dolomite and kaolin catalysts in enhancing fuel production through cigarette waste pyrolysis.^[9] The outcomes revealed that the dolomite catalyst elevated the fuel's calorific value by over 5 MJ/kg, whereas the kaolin catalyst more than halved the fuel viscosity. Both these catalysts occur naturally, rendering them cost-effective choices. Employing these

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catalysts for plastic waste pyrolysis, as opposed to synthetic counterparts, is likely to result in decreased production costs. Liquid fuel from plastic waste is continuously tested in engines to study engine performance and emissions.^[13-20] In most cases, the liquid fuel from plastic waste is treated for quality improvement before being tested in engines.^[13-15,21] The produced fuel still has some properties or characteristics that are not 100% suitable for use in engines. Which test results using liquid fuel from plastic waste in the engine 100% showed that horsepower decreased smoke, nitrogen oxides and carbon monoxide clearly increased.^[16] The liquid fuel from plastic waste, it was found that it significantly reduced carbon monoxide and hydrocarbon emissions from the engine.^[14] However, the reprocessing of liquid fuel from plastic waste increases the time and cost of the production process. If the liquid fuel can be produced from plastic waste to a quality like petroleum fuel in one step for use in engines. It will help reduce the time and cost of the production process. Thus, this research focuses on investigating the pyrolysis of polyethylene bags (PE), polypropylene (PP), and high-density polyethylene (HDPE) using ZSM-5, dolomite, and kaolin catalysts at a reaction temperature of 500°C, aimed at enhancing fuel properties. The fuel properties were analyzed, including heating value, density, viscosity, flash-fire point, cloud point, pour point, acid number, and chemical composition. Furthermore, the performance and emissions of this fuel were tested in an engine.

2. Materials and Methods

2.1 Plastic waste feedstock

Plastic waste samples employed in this research include high-density polyethylene (HDPE), polyethylene (PE), and polypropylene (PP) as shown in Fig. 1 Plastic waste that is

washed and dried in the sun.

2.2 Catalyst

Three types of catalysts in Fig. 2, ZSM-5 (565 \$/kg), dolomite (0.45 \$/kg) and kaolin (0.36 \$/kg) were calcined 4 h at 500 °C.^[22] The experiment of plastic pyrolysis for 1 kg of catalyst was applied to hot filter. The catalysts composed of ZSM-5, dolomite, and kaolin from Brunauer-Emmett-Teller (BET) Belsorp-mini has properties illustrate in Table 1.



Fig. 1 Plastic waste samples (a) PE, (b) PP and (c) HDPE.

2.3 The plastic pyrolysis apparatus

The plastic pyrolysis was conducted using a tabular reactor (fixed-bed which was assembled at Department of Mechanical Engineering, Faculty of Engineering and Industrial Technology, Kalasin University, Thailand). The plastic pyrolysis unit in Fig. 3 components were a reactor, hot filter, condenser, and an electrostatic precipitator (ESP). The plastic pyrolysis system of machine was controlled by automation. The reactor was constructed using stainless steel (grade 304) with a 250 mm diameter and 700 mm in length. The hot filter made from stainless steel grade 304 diameter was 150 mm and the height of 800 mm. The condenser was a compressor heat exchanger. The ESP operated at 15 kV DC was used the aid of fuel collection.

Table 1. Characteristics of the catalysts.

| Type | Catalysts Calcination Temperature/Time | Bulk density (kg/m ³) | Particle density (kg/m ³) | BET surface area (m ² /g) | Mean pore diameter (nm) | Total pore volume (cm ³ /g) | Si/Al ratio |
|----------|--|---|---|---|-------------------------------|--|----------------|
| ZSM-5 | 500 °C for 4h | 600 | 1,043 | 15.8 | 22.1 | 7.62×10 ⁻² | 14.43 |
| Dolomite | 500 °C for 4h | 1,128 | 1,728 | 32.6 | 13.7 | 0.20 | N/A |
| Kaolin | 500 °C for 4h | 687 | 1,074 | 12.2 | 38.1 | 0.18 | N/A |



Fig. 2 The catalyst, (a) ZSM-5, (b) dolomite, and (c) kaolin.

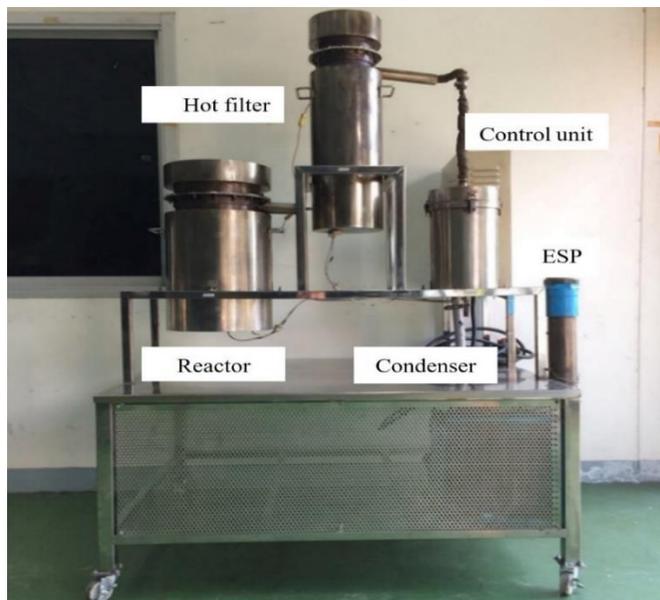


Fig. 3 Plastic pyrolysis unit.

2.4 Catalytic pyrolysis of plastic waste experiments

The pyrolysis temperatures were measured, and controlled control unit (Fig. 4) set at 500°C for reactor and hot filter. The pyrolysis experiments, ZSM-5, dolomite, and kaolin catalysts of 1 kg were used catalytic in a hot filter. For every experiment, approximately 1 kg of plastic waste was put in the reactor. The total experimental run duration for 2 hours. Upon completion of the pyrolysis reaction, the hot components were removed and placed to cool down. Then, the reactor, hot filter and ESP unit were dismantled and weighed for mass balance calculation.

2.5 Mass balance

Biofuel, ash, and gases (non-condensable) were the main composition of products derived from plastic pyrolysis process. These components (except for gases) were separated by means of filtration, weighted, and used to calculate yield of the pyrolysis system. The biofuel yield was calculated from the weight of liquid product obtained from the condenser and the ESP. The ash yields included solid material obtained from hot filter and the tubular reaction, while gas yield was determined as the difference between the other yields and the total weight after reaction.

$$Y_{Fuel} = \frac{(W_{ESP} + W_{Fuel\ pot})}{W_{plastic\ waste}} \times 100 \quad (1)$$

$$Y_{Ash} = \frac{(W_{Reactor} + W_{Hot\ filter} + W_{Gas\ line})}{W_{plastic\ waste}} \times 100 \quad (2)$$

$$Y_{Gas} = 100 - Y_{Fuel} - Y_{Ash} \quad (3)$$

when

Y_{Fuel} = Yields of fuel, wt%

Y_{Ash} = Yields of ash, wt%

Y_{Gas} = Yields of gas, wt%

W_{ESP} = Wet of electrostatic precipitator, g

$W_{Fuel\ pot}$ = Wet of fuel pot, g

$W_{plastic\ waste}$ = Wet of plastic waste, g

$W_{Reactor}$ = Wet of reactor, g

$W_{Hot\ filter}$ = Wet of hot filter, g

$W_{Gas\ line}$ = Wet of gas line, g

2.6 Analyzing fuel properties

The fuel from all three plastics were analyzed by standard properties in Table 2.

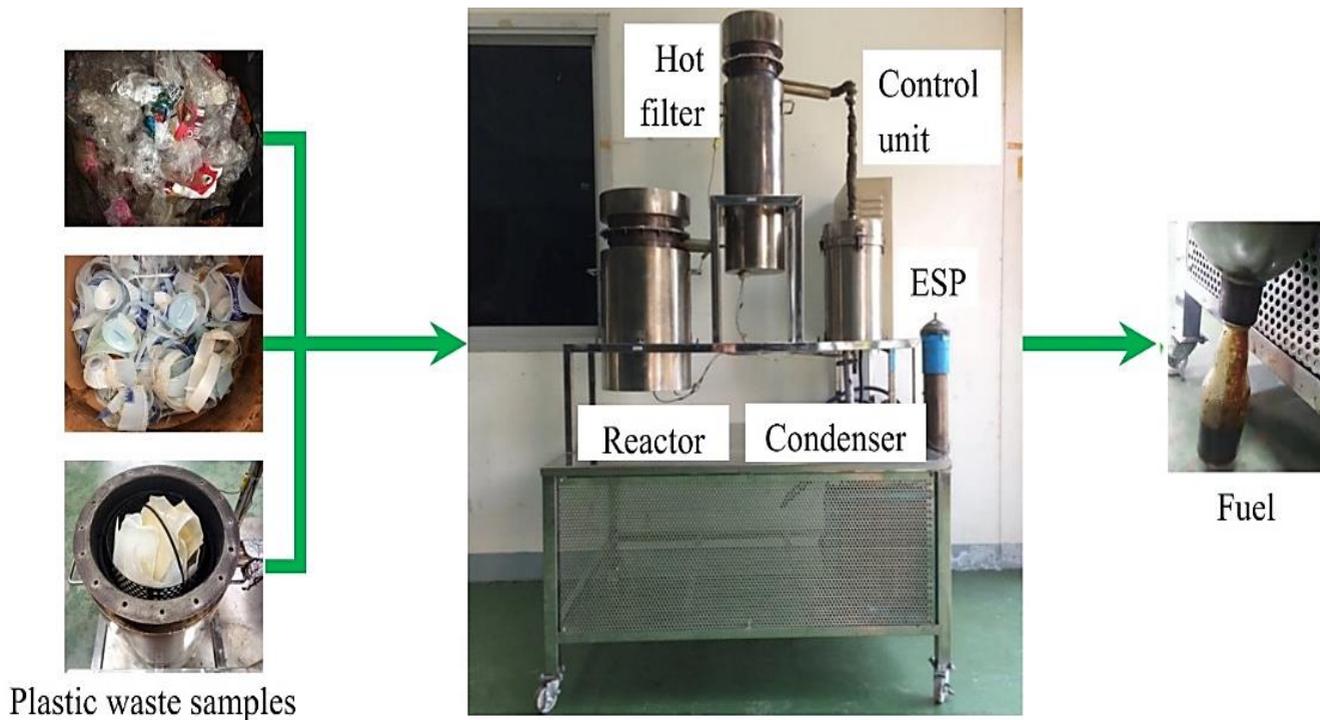


Fig. 4 Experiment of plastic pyrolysis.

Table 2. Properties analysis of biofuel derived from pyrolysis of waste plastic.

| Analysis | Standard | The instruments |
|----------------------------|------------|------------------------------|
| Higher heating value (HHV) | DIN 51900 | Torino Bomb Calorimeter |
| Density | ASTM D4052 | Digital Scales |
| Viscosity | ASTM D445 | Kinetic Viscosity Analyzer |
| Flash point - Fire point | ASTM D93 | Flash point - Fire point Set |
| Pour point | ASTM D97 | Pour point CPP-5Gs |
| Cloud point | ASTM D2500 | Cloud point CPP-5Gs |
| Acid number | ASTM D 974 | Digital Scales |
| Chemical composition | GC/MS | Shimadzu GC/MS-QP2010 |

2.6.1 Calculating HHV

The standard DIN 51900 was employed to calculate the higher heating value (HHV) of biofuel produced during the pyrolysis reaction. The device used for this analysis was the Torino bomb calorimeter (S.M.D). The sample (1 g) was prepared and transferred to a stainless-steel pan, then combusted under 25 bar pressure. The pan was placed inside a container with 2L water. Combustion was initiated by ignition of conductive wire and the run time was set for 20 minutes.

2.6.2 Density

The ASTM D4052 standard was used to find the fuel density of the biofuel. According to the protocol, the samples were measured in a 5 mL cylinder and at 15 °C temperature.

2.6.3 Viscosity

The viscosity analysis was according to ASTM D445. The viscosity was analyzed under 40 °C and a glass tube size 350 (Cannon-Fenske Viscometer).

2.6.4 Flash point - Fire point

The ASTM D93 standard was utilized to find flash and fire point of the produced biofuel. Flash point is defined as the minimum temperature that can result in formation of flame from the fuel. Fire point is defined as the minimum temperature that can cause a continuous fire.

2.6.5 Pour point

Pour point analysis marks formed according to ASTM D97 by first filling the sample vial to the specified volume mark. Put the tube in the injector of pour point meter. Insert the probe used to analyze pour point. And close the test chamber with a pour point probe and press start to start the system. Finally, read the analyzed values and record the results.

2.6.6 Cloud point

The cloud point analysis was performed in accordance with ASTM D2500 with the same analytical procedure as pour point analysis. The cloud point is the temperature at which the wax begins to crystallize, so the temperature is slightly higher than the pouring point. This point is especially important for diesel fuel. The egg begins to crystallize out, it can cause the pot to filter quickly. As a result, the oil cannot be pumped even

though the oil still flows well.

2.6.7 Acid number

Analyze according to ASTM D 974. The solvent was prepared by dosing 495 ml of isopropanol mixed with 500 ml of toluene and 5 ml of distilled water for a volume of 1000 ml. The prepare a standard solution of 0.1 molar concentration of potassium hydroxide in 1000 ml of iso-propanol and weigh about 10.0XXX g of oil. The sample solvent was added to 100 mL of oil and phenolphthalein solution was added to 1 mL of isopropanol. Finally, immerse the probe into the sample, then start analyzing.

2.6.8 Chemical composition

Biofuel composition as obtained using the Shimadzu GC/MS-QP2010 chemical structure analyser. The biofuel samples were diluted (1:1) with methanol-dichloromethane solution and filtered using Filtrex nylon filter (2 µm). The column used inside the oven was a Restex Rtx-5MS column (Restex, USA) 0.25 mm in diameter, 30 m long and 0.25 µm thick film with helium as carrier gas at a velocity of 40 m/s. The temperature program used to analyze the composition of biodiesel set at 60 °C hold for 2 minutes to the operating temperature of the system, then ramp up to 270 °C at a heating rate of 5 °C/min and hold for 5 minutes. Electron impact (EI) were used to generate a 70 eV ion source for interface temperatures of 250 °C and 230 °C, supporting mass scanned of 20-260 m/z every 0.5 s. Data from detector was analyzed with a SHIMADZU LabSolutions GC-MS.^[23]

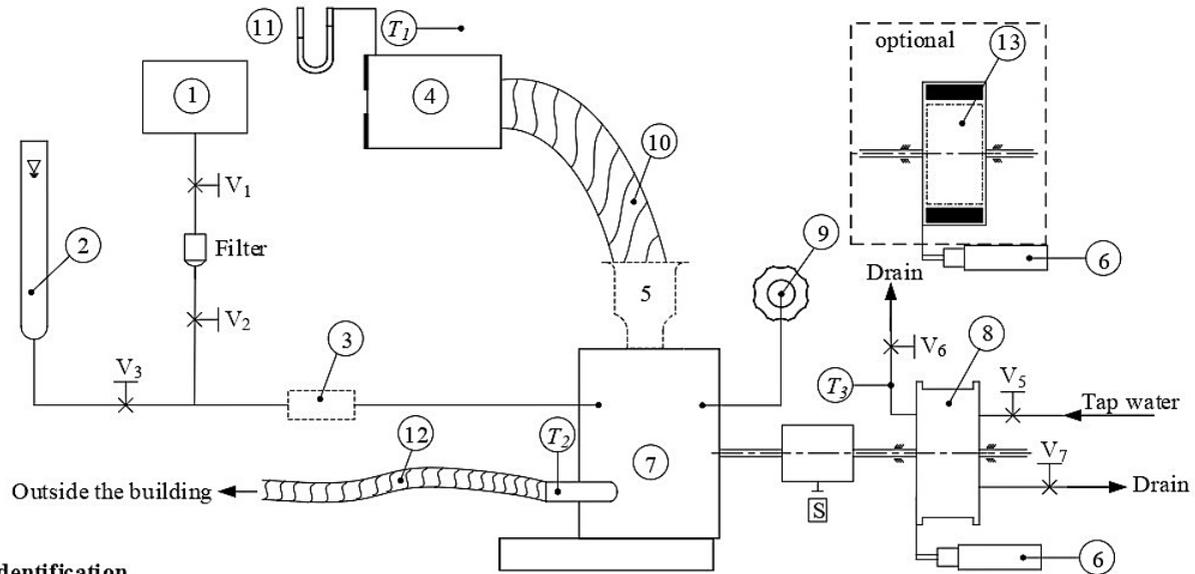
2.7 Test fuel for engine

This research uses a single-cylinder four-stroke diesel engine in Fig. 5. The engine has a displacement of 547 cc, a maximum power of 10.5 HP at a maximum speed of 2400 rpm and a compression ratio of 18: 1. This research was tested carried out at a maximum engine speed of 2400 rpm under a laboratory temperature of 40 °C to determine the brake horsepower and brake specific fuel consumption.

The following equations were used to calculate brake horsepower and brake specific fuel consumption.

Brake horsepower

$$P = \frac{\left(\frac{2\pi T n}{60}\right)}{1,000} \quad (4)$$



Identification

- | | | |
|--|---|--|
| 1) Fuel tank | 8) Dynamometer | T_1) Ambient air temperature |
| 2) Graduated cylinder | 9) Throttle control valve knob | T_2) Exhaust gas temperature |
| 3) Fuel flow sensor (optional) | 10) Engine inlet air duct | T_3) Dynamometer water temperature |
| 4) Differential pressure measuring device | 11) Inclined manometer | V_5) Dynamometer water inlet valve |
| 5) Air flow sensor (optional alternative to 4) | 12) Exhaust hose (optional) | V_6) Dynamometer vent valve |
| 6) Torque sensor | 13) Eddy current dynamometer (optional) | V_7) Dynamometer water Outlet valve |
| 7) Engine | S) Engine speed sensor | |

Fig. 5 Schematic diagram of engine test.

$$BHP = \frac{P}{0.7457}$$

when

P = engine brake power (kW)

T = torque (N-m)

n = engine cycle (rpm)

BHP = brake horsepower (HP)

Fuel consumption

$$Q_{mf} = Q_{vf} \rho_f$$

When Q_{mf} = fuel consumption (kg/s)

Q_{vf} = Volume of fuel (m³/s)

ρ_f = Fuel density (kg/m³)

Brake specific fuel consumption

$$Bsfc = \frac{3600Q_{mf}}{P}$$

when

$Bsfc$ = brake specific fuel consumption (kg/kW.hr)

P = engine brake power (kW)

Q_{mf} = fuel consumption (kg/s)

2.8 Analysis of engine emissions

This research analyzes emissions of the engine with a car exhaust meter and analyzer brand CAPELEC model CAP-3201-GO has the following details.

- Display HC value 0-20000 PPM
- Display CO value 0-5% vol
- Display Corrected CO: 0-10% vol
- Displays NO_x values from 0-5000 PPM.

- (5) - Displays the engine speed from 0-9999 RPM.
- Atmospheric pressure from 750-1150 mbar
- Respond to measurements within 5 seconds.
- Certified OIML R99 Class 0, ISO-3930 and BAR97

3. Results and discussion

3.1 Plastic waste properties

- (6) **Table 3** shows that the characteristics of the three types of plastic waste are clearly different, with PE plastic waste having the highest volatile matter content of 96.4 wt%, while PP and HDPE plastic waste having 92.1 and 90.6 wt%, respectively. This is because HDPE has the highest ash content of 4.4 wt%, resulting in the lowest content of volatile matter substances. The elemental analysis showed that high volatile matter in the plastic waste had high carbon content and high calorific value.
- (7)

Plastic waste characteristics in **Table 3** can also be used to predict the yield of the product that will occur in the pyrolysis process. Plastic waste that can produce the highest yield of fuel when pyrolysis is PE. This type of waste contains high volatile substances and low ash. Ash is an impediment to pyrolysis in converting raw materials into fuel. In the past, there was a research study on the removal of ash from raw materials with acid. It was found that the ash in raw materials can be reduced by more than 60%.^[24] However, the raw material used in this research is biomass, which is different from the raw material of this research. Therefore, finding a suitable method for

Table 3. Characteristics of plastic waste.

| Feedstock | Proximate analysis (wt% dry basis) | | | Elemental analysis (wt% dry basis) | | | | | HHV (MJ/kg) |
|-----------|---------------------------------------|-----------------|-----|---------------------------------------|------|-----|-----|-----|----------------|
| | Volatile Matter | Fixed Carbon | Ash | C | H | N | S | O* | |
| PE | 96.4 | 2.4 | 1.2 | 86.4 | 12.8 | 0.1 | 0.0 | 0.7 | 36.8 |
| PP | 92.1 | 5.1 | 2.8 | 85.8 | 10.9 | 0.1 | 0.0 | 3.2 | 34.9 |
| HDPE | 90.6 | 5.0 | 4.4 | 83.1 | 8.6 | 0.2 | 0.3 | 7.8 | 33.4 |

* By difference.

disposing of ash in plastic waste is another interesting method for further study in the future.

3.2 Effect of the plastic type to product yields

Figure 6 shows that the PE plastic waste can be processed into fuel yields at a maximum of 57.8 wt%. While, the PP and HDPE plastic waste can be processed into fuel yields, 52.4 and 50.4 wt% respectively. This is because PE plastic waste can process ash and gas content less than PP and HDPE plastic waste. HDPE and PP plastic waste have a higher ash content in the starting feedstock than PE plastic waste. When pyrolysis, this ash cannot decompose into vapor to condense into fuel. HDPE plastic waste can be processed into ash at a maximum yield of 11.7 wt%, while PP and PE plastic waste can be processed into ash in the yields of 10.7 and 8.5 wt%. In addition, the high ash content in the feedstock when pyrolysis results in a high gas yield. It can be observed from the gas yield in Fig. 6 HDPE and PP plastic waste had the highest gas yield of 37.9 and 36.9 wt%, respectively. This is because the ash contained in the feedstock contributes to the secondary cracking.^[23] of the pyrolysis vapor into non-condensable gas. The ash content in feedstock affecting the yield of fuel, ash and gas in this research is consistent with the previous research. It was reported that polyethylene (PE) had ash content of 6.9 wt%, the yields of fuel, ash, and gas have 47, 7 and 46 wt%, respectively. While polystyrene (PS) had an ash content of 0.1 wt%, the yields of fuel, ash and gas has 91, 1 and 8 wt%, respectively.^[25]

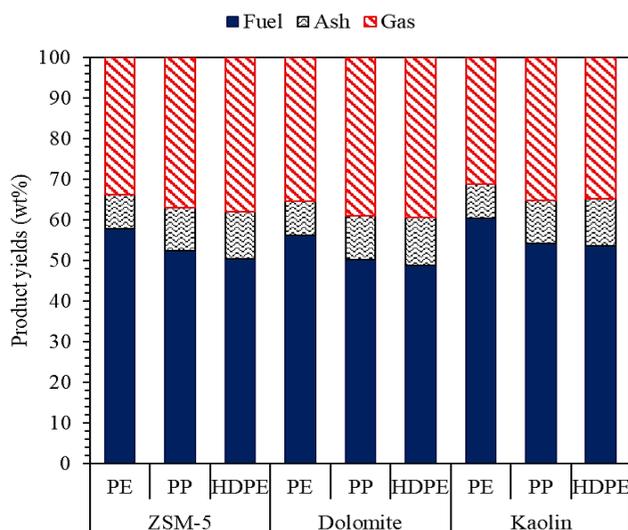


Fig. 6 Type of plastic to product yields.

Upon examining the impacts of the three catalyst types, it was observed that pyrolyzing PE with a kaolin catalyst resulted in the highest fuel yield at 60.4 wt%. Furthermore, when conducting PP and HDPE pyrolysis with this catalyst, significantly greater fuel yields were achieved compared to both ZSM-5 and kaolin catalysts. This disparity arises from the larger pore structure of the kaolin catalyst, which in turn diminishes secondary vapor pyrolysis. Consequently, the product exhibits diminished gas yield. In conclusion, the employment of the kaolin catalyst emerges as the optimal approach for generating fuel from plastic waste.

Figure 7 shows the physical characteristics of the fuel produced from the three plastics. It shows that all three bottles of fuel are the same color, which is dark brown to almost black. This could explain that the type of plastic does not affect the color of the liquid fuel product produced.



Fig. 7 Fuel from plastic waste (a) PE (b) PP (c) HDPE.

The fuel from plastic waste in this research has a rather pungent odor compared to diesel fuel. This may be due to the diversity of the chemical composition of this fuel. This could be the result of ingredients added to plastics before they end up in waste. However, the physical characteristics of the fuel in this study are similar to the previous research was dark in color.^[4,14,15] If you want this fuel to be clear yellow, it can be refined to improve the quality before being used for real use. In the past, research has been carried out to improve the quality of this fuel. It has properties similar to that of the diesel fuel, such as the thermal cracking process^[14] and controlling

condensation temperature.^[8]

3.3 Effect of the plastic type on fuel properties.

The fuel properties of the three plastics in Table 4, show that PE plastic waste produced the highest high heating value (HHV) of fuel, 42.7 MJ/kg. This is because this fuel has a higher chemical composition of certain hydrocarbon groups than PP and HDPE fuels such as 1-Undecene (C₁₁H₂₂), Undecane (C₁₁H₂₄), 1-Dodecene (C₁₂H₂₄), 1-Tetradecene (C₁₄H₂₈) and Tetradecane (C₁₄H₃₀). Which of these chemicals are classified in the group of diesels. It is well known that the chemical constituents of the diesel group were higher calorific values than the benzene group. Achieve a high calorific value, this fuel may be distilled to increase the purity of these chemical constituents. It has been reported that improving the purity of plastic waste fuel has resulted in the color and calorific value of this fuel similar to that of diesel fuel.^[14]

The PP fuel has a maximum density of 892.3 kg/m³ resulting in a minimum viscosity of 0.8 cSt. This is because chemical constituents such as 1-Undecene (C₁₁H₂₂), Undecane (C₁₁H₂₄), 1-Dodecene (C₁₂H₂₄), 1-Tetradecene (C₁₄H₂₈) and Tetradecane (C₁₄H₃₀) have a large molecular weight. In particular, the Tetradecane (C₁₄H₃₀) has a high molecular weight of 198.39 g/mol.^[26] The data clearly show that the chemical composition greatly improves the calorific value, density, and viscosity of the fuel from plastic waste.

Table 4 shows that HDPE fuels have the lowest flash and fire points of 5.3 and 18.1 °C. As a result of this fuel has a higher chemical composition in the C₇-C₉ benzene group up to 34.7%. Table 4 clearly shows that the chemical composition of the HDPE fuel was 1-Heptene (C₇H₁₄), Heptane (C₇H₁₆), Heptane, 4-methyl- (C₈H₁₄), 1-Octene (C₈H₁₆), Octane (C₈H₁₈) and Cyclononane (C₉H₁₈). It is known that gasoline ignites at a lower temperature compared to diesel. The flash point of this fuel is in the same range as that of the same plastic waste fuel. The pyrolysis with a natural zeolite catalyst at a reaction temperature of 450 °C.^[10]

Pour point is another property used to measure the quality of fuel. Fuel with low pour point is suitable for use as fuel in

the engine. Table 4, shows that PE fuel has the lowest pour point of 8 °C compared to PP and HDPE fuel. It has a very low pour point compared to the same type of fuel obtained by pyrolysis with natural zeolite catalysts. It was found that the fuel had a pour point of 24 °C.^[10] This is due to the high density of this fuel because of its heavy molecules and high content of acids. This fuel has a high acid content of 0.18 wt%. It is expected that this acid helps the fuel to flow more smoothly. The acids detected in this fuel are n-Hexadecanoic acid (C₁₆H₃₂O₂) and Octadecanoic acid (C₁₈H₃₆O₂). This acid can be a problem for this fuel's pungent odor. This should be improved before being used to increase the quality of the fuel. In which most of the fuel obtained from plastic pyrolysis still contain these acids.^[6]

The cloud point is the lower temperature at which a solution is transparent through liquid-liquid phase separation to form an emulsion. Includes liquid-solid phase transition to form stable soils or precipitated suspensions. Table 4 shows that HDPE fuel has the lowest cloud point in plastic waste fuel. It is expected that the chemical composition of benzene mixed in this fuel will increase the performance of the liquid phase separation more quickly.

When comparing the properties of fuels as shown in Table 4, fuels from all three types of plastics waste have lower calorific value than diesel fuel. This is because the fuel obtained from all plastic contains a mixture of chemical elements in the benzene, diesel, and acid group. The density of fuel from all three plastics was in the same range as that of diesel fuel. However, the chemical constituents of benzene group in the plastic fuel make it more than twice as low in viscosity as that of diesel. Also, this plastic fuel is approximately twice as flammable as diesel fuel.

The fuel properties as depicted in Table 4, originating from the three distinct catalysts, reveal that the fuel obtained via the kaolin catalyst manifests the lowest calorific value. Comparatively, the fuel resulting from the dolomite catalyst exhibits a slightly reduced calorific value. This observation signifies that these natural catalysts, namely kaolin and dolomite, do not yield as substantial an enhancement in

Table 4. Properties of fuel.

| Properties | Diesel | ZSM-5 | | | Dolomite | | | Kaolin | | |
|---|--------|-------|-------|-------|----------|-------|-------|--------|-------|-------|
| | | PE | PP | HDPE | PE | PP | HDPE | PE | PP | HDPE |
| High heating value (MJ/kg) | 43.8 | 42.2 | 41.8 | 40.7 | 40.2 | 39.6 | 37.8 | 39.2 | 38.6 | 37.1 |
| Bulk density at 15°C (kg/m ³) | 867.2 | 892.3 | 816.8 | 842.4 | 883.4 | 835.1 | 871.2 | 864.7 | 826.4 | 872.6 |
| Kinematic viscosity at 40°C (cSt) | 2.8 | 0.8 | 1.1 | 1.0 | 0.5 | 0.7 | 0.4 | 1.4 | 1.3 | 1.4 |
| Flash point (°C) | 56.4 | 7.5 | 7.3 | 5.3 | 8.1 | 8.3 | 7.7 | 7.8 | 8.2 | 7.6 |
| Fire point (°C) | 62.5 | 25.7 | 24.6 | 18.1 | 26.1 | 23.8 | 24.9 | 25.2 | 23.8 | 22.7 |
| Pour point (°C) | 3.2 | 8.0 | 11.8 | 9.9 | 8.3 | 8.1 | 9.2 | 8.5 | 8.1 | 8.7 |
| Cloud point (°C) | -10.8 | 24.5 | 25.5 | 22.8 | 23.7 | 24.3 | 25.1 | 26.7 | 21.8 | 22.6 |
| Acid value mg KOH/g oil | <0 | 0.36 | 0.05 | 0.21 | 0.12 | 0.02 | 0.11 | 1.13 | 0.73 | 0.94 |
| Acid content (wt%) | <0 | 0.18 | 0.03 | 0.11 | 0.07 | 0.01 | 0.03 | 0.82 | 0.37 | 0.71 |

fuel calorific value as the ZSM-5 catalyst. Nonetheless, when evaluating other fuel properties, it becomes evident that the dolomite catalyst drastically diminishes fuel viscosity to a minimum of 0.4 cSt and reduces acidity to merely 0.01% wt%. [Table 5](#) shows that the chemical composition of fuel from plastic waste is different from that of diesel fuel. The chemical composition of plastic waste fuel is benzene, diesel, and acid group. The chemical composition of plastic waste fuel was found that Cyclononane (C₉H₁₈) and 1-Dodecene (C₁₂H₂₄) were the main constituents of this fuel. The HDPE plastic waste can produce up to 20.3% of the chemical composition Cyclononane (C₉H₁₈). While PE plastic waste can produce up to 27.1% of the chemical composition 1-Dodecene (C₁₂H₂₄).

Plastic waste oil obtained in this study is free of acidic components, namely n-Hexadecanoic acid (C₁₆H₃₂O₂) and Octadecanoic acid (C₁₈H₃₆O₂). The acid content in the chemical composition of this fuel corresponds to the results of the analysis of fuel properties in [Table 5](#). The analysis clearly shows that PE fuel has the highest acid composition of 0.4%. While PP fuel has a minimum acid composition of 0.2%. However, the acidic content of the fuel contained in this plastic waste is very small compared to biomass pyrolysis fuel, which

has an acidic content of more than 3.7%.^[23]

The chemical constituents of this acid can be eliminated by increasing the condenser temperature.^[8] In this paper, it was described that increasing the condenser temperature causes the chemical constituents of the acid in the pyrolysis vapor to escape with the non-condensable gas during the production process. The analysis of the chemical composition of the fuel from plastic waste found that the acidic chemical composition of the fuel was not found.

[Figure 8](#) clearly shows that diesel fuel has the main chemical constituent, Heneicosane (C₂₁H₄₄), which is as high as 36.3%. While the fuel from plastic waste has the highest chemical composition, 1-Dodecene (C₁₂H₂₄). The peak ID range 1-8 was C7-C10, detectable in fuel derived from plastic waste.

Presented in [Table 6](#) is the chemical composition of the fuel derived from PE after pyrolysis utilizing the three distinct catalysts. The data indicates a notable disparity, with both dolomite and kaolin catalysts yielding considerably higher benzene compound proportions compared to the ZSM-5 catalyst. Specifically, the dolomite catalyst generates Cyclononane at an impressive 20.3% rate. However, it's

Table 5. Chemical composition in the fuel from ZSM-5 catalyst.

| Peak ID | Compound name | Formula | Chromatographic peak area (%) | | | |
|----------------|-----------------------|--|-------------------------------|------|------|------|
| | | | Diesel | PE | PP | HDPE |
| 1 | 1-Heptene | C ₇ H ₁₄ | 0.0 | 2.1 | 1.6 | 2.8 |
| 2 | Heptane | C ₇ H ₁₆ | 0.0 | 2.0 | 3.4 | 2.5 |
| 3 | Heptane, 4-methyl- | C ₈ H ₁₄ | 0.0 | 2.2 | 1.4 | 2.5 |
| 4 | 1-Octene | C ₈ H ₁₆ | 0.0 | 2.2 | 2.1 | 3.1 |
| 5 | Octane | C ₈ H ₁₈ | 0.0 | 2.7 | 1.4 | 3.5 |
| 6 | Cyclononane | C ₉ H ₁₈ | 0.0 | 16.7 | 18.0 | 20.3 |
| 7 | 1-Decene | C ₁₀ H ₂₀ | 0.0 | 3.0 | 3.6 | 7.0 |
| 8 | Octane, 3,3-dimethyl- | C ₁₀ H ₂₂ | 0.0 | 5.7 | 6.5 | 1.4 |
| 9 | 1-Undecene | C ₁₁ H ₂₂ | 1.4 | 3.5 | 1.6 | 2.9 |
| 10 | Undecane | C ₁₁ H ₂₄ | 6.9 | 3.7 | 2.8 | 2.0 |
| 11 | 1-Dodecene | C ₁₂ H ₂₄ | 9.0 | 27.1 | 24.5 | 21.5 |
| 12 | Dodecane | C ₁₂ H ₂₆ | 0.0 | 2.7 | 3.6 | 1.3 |
| 13 | 1-Tridecene | C ₁₃ H ₂₆ | 2.7 | 3.8 | 5.2 | 1.8 |
| 14 | 1-Tetradecene | C ₁₄ H ₂₈ | 1.7 | 3.4 | 1.6 | 1.3 |
| 15 | Tetradecane | C ₁₄ H ₃₀ | 16.2 | 5.7 | 2.1 | 2.5 |
| 16 | 1-Pentadecene | C ₁₅ H ₃₀ | 8.1 | 2.5 | 2.2 | 4.4 |
| 17 | Pentadecane | C ₁₅ H ₃₂ | 14.2 | 1.9 | 1.6 | 2.3 |
| 18 | Hexadecane | C ₁₆ H ₃₄ | 1.5 | 1.8 | 6.3 | 3.4 |
| 19 | 1-Heptadecene | C ₁₇ H ₃₄ | 1.1 | 0.2 | 1.5 | 3.2 |
| 20 | Heptadecane | C ₁₇ H ₃₆ | 0.8 | 1.8 | 1.7 | 2.2 |
| 21 | Octadecane | C ₁₈ H ₃₈ | 0.0 | 1.5 | 1.3 | 1.1 |
| 22 | Heneicosane | C ₂₁ H ₄₄ | 36.3 | 0.5 | 2.8 | 4.5 |
| 23 | 1,19-Eicosadiene | C ₂₀ H ₃₈ | 0.1 | 2.7 | 3.0 | 2.1 |
| 24 | n-Hexadecanoic acid | C ₁₆ H ₃₂ O ₂ | 0.0 | 0.3 | 0.1 | 0.2 |
| 25 | Octadecanoic acid | C ₁₈ H ₃₆ O ₂ | 0.0 | 0.1 | 0.1 | 0.1 |
| Total area (%) | | | 100 | 100 | 100 | 100 |

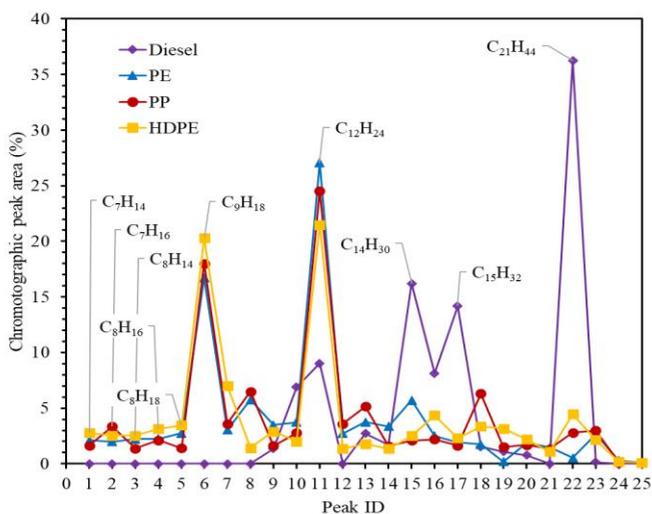


Fig. 8 Chromatographic peak area of the fuel from ZSM-5 catalyst.

noteworthy that the chemical constituents within the diesel category are comparatively fewer when contrasted with pyrolysis involving the ZSM-5 catalyst. This disparity explains the diminished calorific value in fuels derived from

the dolomite catalyst and kaolin clay. It is common knowledge that gasoline exhibits flammability and a calorific value lower than that of diesel.

Figure 9 vividly illustrates that both dolomite and kaolin catalysts yield a more abundant benzene chemical composition in comparison to the ZSM-5 catalyst. Notably, the dolomite catalyst significantly facilitates the highest augmentation in C₉H₁₈. Upon scrutinizing peaks 24-25, it becomes evident that the dolomite catalyst boasts the most prominent peak. This peak corresponds to a chemical component within the acid group. This observation signifies that the fuel tends to become more acidic when engaging in the pyrolysis of plastic waste characterized by a larger pore size.

3.4 Effect of the plastic type to brake horsepower (BHP) and brake specific fuel consumption (BSFC)

Fuel test results on a 10.5 HP single-cylinder diesel engine in Fig. 10 show that diesel fuel results in a maximum engine brake horsepower of 10.5 HP. When tested with fuel from all three types of plastic waste, the brake horsepower was significantly reduced. Engine test results with fuel from HDPE

Table 6. Chemical composition in the fuel from catalysts.

| Peak ID | Compound name | Formula | Chromatographic peak area (%) | | | |
|----------------|-----------------------|--|-------------------------------|-------|----------|-------|
| | | | Diesel | ZSM-5 | Dolomite | Kolin |
| 1 | 1-Heptene | C ₇ H ₁₄ | 0.0 | 2.1 | 2.4 | 3.8 |
| 2 | Heptane | C ₇ H ₁₆ | 0.0 | 2.0 | 3.0 | 4.5 |
| 3 | Heptane, 4-methyl- | C ₈ H ₁₄ | 0.0 | 2.2 | 3.7 | 5.5 |
| 4 | 1-Octene | C ₈ H ₁₆ | 0.0 | 2.2 | 4.6 | 6.1 |
| 5 | Octane | C ₈ H ₁₈ | 0.0 | 2.7 | 2.8 | 3.5 |
| 6 | Cyclononane | C ₉ H ₁₈ | 0.0 | 16.7 | 18.0 | 20.3 |
| 7 | 1-Decene | C ₁₀ H ₂₀ | 0.0 | 3.0 | 2.4 | 2.0 |
| 8 | Octane, 3,3-dimethyl- | C ₁₀ H ₂₂ | 0.0 | 5.7 | 5.1 | 4.4 |
| 9 | 1-Undecene | C ₁₁ H ₂₂ | 1.4 | 3.5 | 2.6 | 2.7 |
| 10 | Undecane | C ₁₁ H ₂₄ | 6.9 | 3.7 | 3.4 | 2.0 |
| 11 | 1-Dodecene | C ₁₂ H ₂₄ | 9.0 | 27.1 | 26.8 | 21.5 |
| 12 | Dodecane | C ₁₂ H ₂₆ | 0.0 | 2.7 | 2.4 | 1.3 |
| 13 | 1-Tridecene | C ₁₃ H ₂₆ | 2.7 | 3.8 | 3.2 | 1.8 |
| 14 | 1-Tetradecene | C ₁₄ H ₂₈ | 1.7 | 3.4 | 2.7 | 1.3 |
| 15 | Tetradecane | C ₁₄ H ₃₀ | 16.2 | 5.7 | 5.2 | 2.5 |
| 16 | 1-Pentadecene | C ₁₅ H ₃₀ | 8.1 | 2.5 | 2.2 | 1.4 |
| 17 | Pentadecane | C ₁₅ H ₃₂ | 14.2 | 1.9 | 1.6 | 1.4 |
| 18 | Hexadecane | C ₁₆ H ₃₄ | 1.5 | 1.8 | 1.3 | 1.0 |
| 19 | 1-Heptadecene | C ₁₇ H ₃₄ | 1.1 | 0.2 | 0.2 | 1.1 |
| 20 | Heptadecane | C ₁₇ H ₃₆ | 0.8 | 1.8 | 1.7 | 2.2 |
| 21 | Octadecane | C ₁₈ H ₃₈ | 0.0 | 1.5 | 1.3 | 1.1 |
| 22 | Heneicosane | C ₂₁ H ₄₄ | 36.3 | 0.5 | 0.2 | 1.5 |
| 23 | 1,19-Eicosadiene | C ₂₀ H ₃₈ | 0.1 | 2.7 | 2.3 | 2.2 |
| 24 | n-Hexadecanoic acid | C ₁₆ H ₃₂ O ₂ | 0.0 | 0.3 | 0.5 | 2.4 |
| 25 | Octadecanoic acid | C ₁₈ H ₃₆ O ₂ | 0.0 | 0.1 | 0.4 | 2.5 |
| Total area (%) | | | 100 | 100 | 100 | 100 |

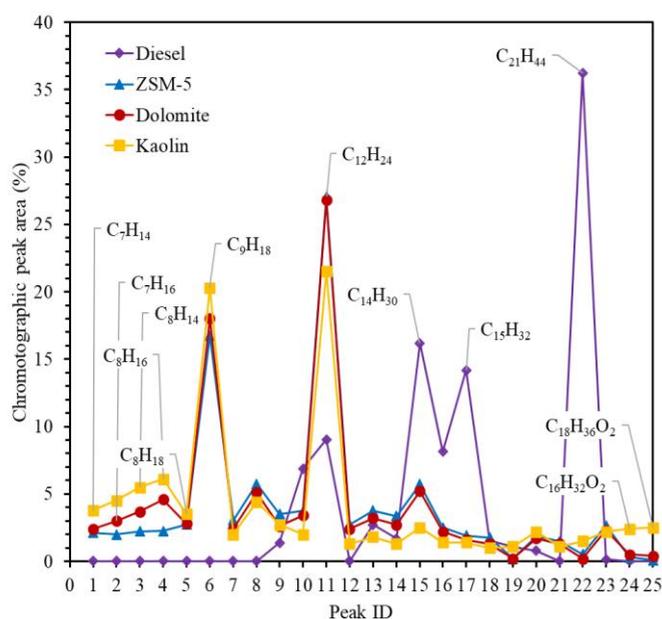


Fig. 9 Chromatographic peak area of the fuel from catalysts.

plastic waste, engine brake horsepower reduced to a minimum of 9.1 HP. While the engine test results with fuel from PE and PP plastic waste, the brake horsepower was 10.0 and 9.7 HP, respectively.

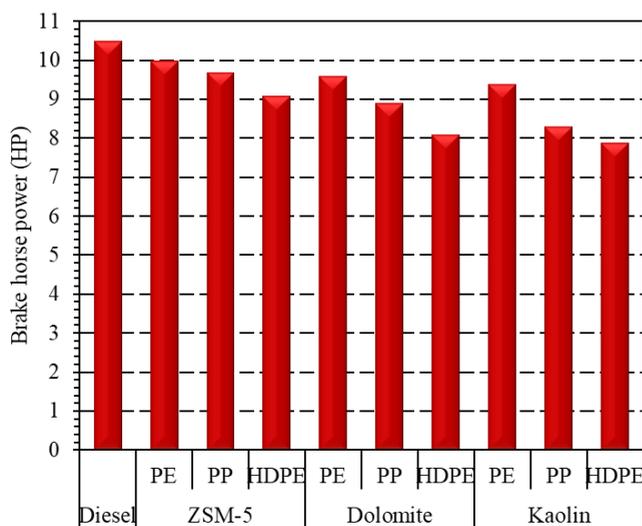


Fig. 10 Type of plastic to brake horsepower of engine.

Engine brake horsepower is reduced due to the use of this plastic waste fuel because of the chemical composition of the fuel. The plastic waste fuel contains a high chemical composition of the benzene group, resulting in lower calorific value than diesel fuel. When testing the engine with plastic waste fuel, the thermal efficiency generated inside the engine cylinders was low. The fuel from HDPE plastic waste has the highest chemical composition in the benzene group, 34.7%. It has the lowest in-cylinder thermal efficiency, resulting in the lowest brake horsepower. It has been reported that mixing plastic waste fuel with diesel fuel at different ratios resulted in lower fuel calorific value and lower brake horsepower.^[21]

When the brake horsepower generated by the pyrolysis of the three catalysts is compared, a noticeable disparity emerges. The catalysts of natural dolomite and kaolin exhibit notably diminished results. This discrepancy stems from the fact that these two catalysts yield fuel possessing reduced calorific values. In particular, the kaolin catalyst, when employed in the pyrolysis of HDPE, produces fuel characterized by the most modest calorific value, measuring at 37.1 MJ/kg. Consequently, the engine experiences a minimal brake horsepower of 7.9 HP.

This outcome can be attributed to the chemical composition within the benzene group. This composition not only results in a diminished calorific value for the fuel but also leads to a discernible reduction in braking horsepower. This observation aligns with the findings presented by Yilmaz *et al.*^[18] Their study reveals that the introduction of low-heat waste oil-derived biodiesel into diesel, in varying proportions from 5% to 35%, leads to a progressive decline in engine brake thermal efficiency. The efficiency diminishes from an initial value of 21.35% to a final figure of 19.14%.

The low calorific value of fuel results in lower thermal efficiency, lower brake horsepower and higher fuel consumption. Fig. 11 clearly shows that fuel from HDPE plastic waste has a maximum brake specific fuel consumption of 1.57 kg/kW.hr. Which is approximately 0.45 kg/kW.hr. higher than the diesel test. This is because HDPE plastic waste fuel has a calorific value of 40.7 MJ/kg, while PE, PP and diesel fuel have a calorific value of 42.2, 41.8 and 43.8 MJ/kg respectively. This is in line with previous research that reported that fuel with low calorific value will increase the brake specific fuel consumption.^[21] Therefore, if wanting to increase horsepower and reduce fuel consumption, fuel properties should be improved by reducing the chemical composition in the benzene and acid groups.

The figures depicted in Fig. 11 unmistakably illustrate that both the dolomite and kaolin catalysts exhibit a brake specific fuel consumption surpassing that of the ZSM-5 catalyst. This discrepancy is a direct consequence of the decreased brake horsepower. Consequently, if the objective is to curtail the pace of fuel consumption, it becomes imperative to extract the chemical constituents within the benzene group from the fuel prior to its utilization within the engine.

3.5 Effect of fuel type on engine emissions

Diesel engine exhaust emissions into the atmosphere include Hydrocarbons (HC), Carbon Monoxide (CO), and Nitrogen Oxides (NO_x). The HC gas in diesel engine exhaust is caused by the combustion of hydrocarbons in the fuel. If the HC gas in the engine exhaust system is high, it indicates that the hydrocarbons in that fuel cannot burn completely, resulting in black smoke and foul odors. For CO gas, it occurs due to incomplete combustion due to insufficient oxygen supply for combustion. The NO_x is formed by reacting nitrogen with hydrocarbons or nitrogen with oxygen at high temperatures in the combustion chamber of an engine.

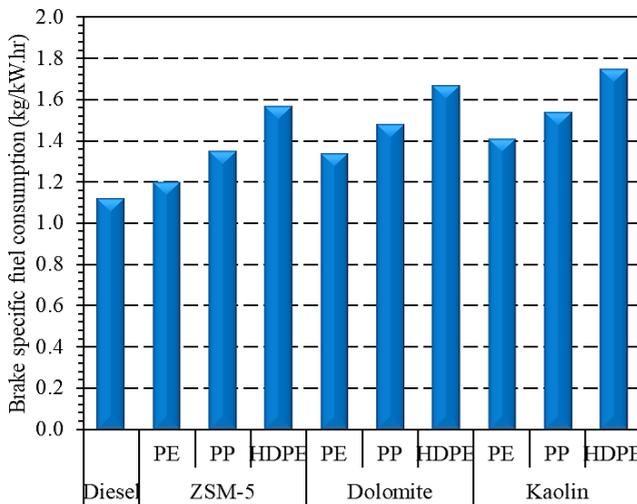


Fig. 11 Type of plastic to brake specific fuel consumption.

Figure 12 shows that diesel fuel when tested in a diesel engine contains HC 22.5 ppm, which is in the range of HC emission standards for conventional diesel engines in the range of 20-300 ppm. Testing the engine with all three plastic waste fuels gave the diesel engine more than four times lower HC gas than the diesel fuel test. The fuel from HDPE plastic waste has a minimum HC emission of 4.2 ppm. This is expected to be a result of the fuel from plastic waste containing a mixture of chemical components in the benzene group. The burned of hydrocarbons completely and thoroughly within the combustion chamber. Fuel from plastic waste therefore increases the efficiency of combustion more completely.^[14] While diesel engines rely on the principle of heating the cylinder and injecting fuel into the ignition.

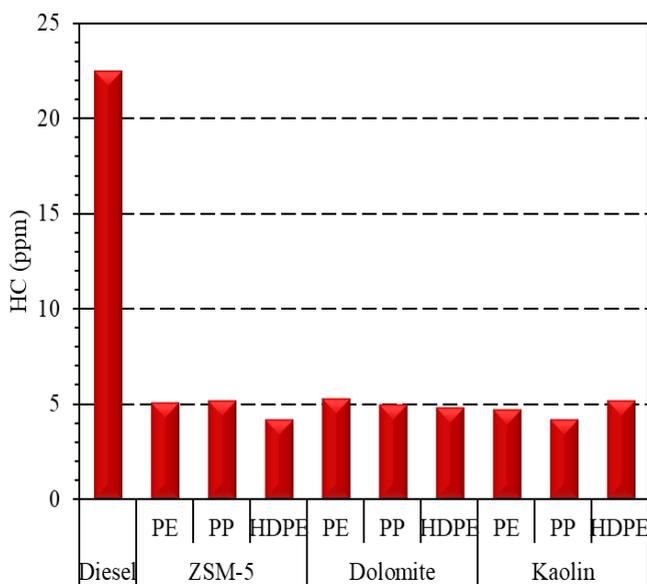


Fig. 12 HC emissions.

Therefore, the presence of the chemical composition of the benzene group in the fuel helps the fuel to ignite easily and covers the combustion chamber. As a result, the amount of HC gas emitted through the exhaust gas is low. The research also

found that fuel from plastic waste when tested in a diesel engine was smokeless and odorless.

All three catalyst types depicted in Fig. 12 exhibited comparable HC levels within the range of 4–5 ppm. This observation indicates that variations in the quantity of benzene-related chemical constituents within the fuel do not exert an influence on HC emissions. Consequently, it can be concluded that natural catalysts possess the capacity to generate fuel that mitigates the pollution stemming from combustion processes within engines.

The amount of CO in the engine exhaust gases is an indicator of the combustion efficiency of this fuel. Fig. 13 shows that diesel fuel when tested in a single-cylinder engine has a maximum CO emission of 0.058 %vol. The theory of engine compression (Air/Fuel) 15:1 CO emissions in the exhaust gas must not exceed 1 %vol. The single-cylinder diesel engine tested in this research has a compression ratio of (Air/Fuel) 18:1. The CO content measured in the engine exhaust fell within the range specified by the internal combustion theory.

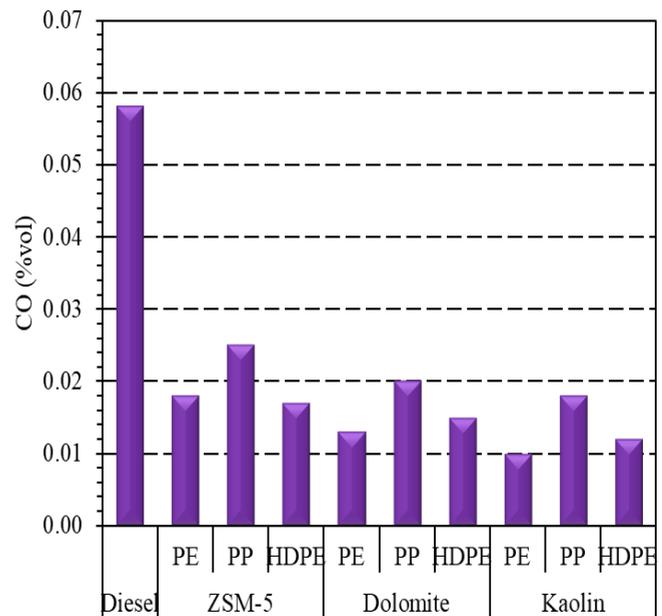


Fig. 13 CO emissions.

The measurement results of the CO content in the engine exhaust as shown in Fig. 13 show that the fuel from the three types of plastic waste significantly reduced the CO content in the engine exhaust. The fuel from HDPE plastic waste reduces the amount of CO in the engine exhaust to as low as 0.017 %vol. Which can explain that this type of fuel maximizes the efficiency of combustion in diesel engines. The reduction in engine exhaust CO emissions when using plastic waste oil as fuel is thought to be due to two hypotheses. The first hypothesis in the fuel from plastic waste is the chemical composition of the flammable benzene group, thus allowing complete combustion and covering the combustion chamber. The second hypothesis in the fuel from plastic waste is the chemical composition of oxygen in the acidic form. Therefore,

this oxygen may increase the complete combustion process.^[21] The second assumption can be considered from the fuel from plastic waste PE and PP have the same chemical composition in the benzene group, which is 27.9%. But fuel from PE plastic waste has a maximum acidic chemical composition of 0.4%, resulting in lower CO emissions in engine than using the PP plastic waste fuel.

Figure 13 illustrates a decline in the CO content of fuel produced through the utilization of the kaolin catalyst. Fuels derived from PE exhibit CO levels as minimal as 1 %vol. In the case of this fuel, meticulous analysis revealed its heightened acidity and a pronounced presence of chemical constituents within the acid group. Consequently, the oxygen inherent in these acidic components contributes to achieving more comprehensive combustion, yielding a marked reduction in CO emissions.

However, it's essential to acknowledge that these acidic components might engender enduring consequences for engine components. Should prolonged and practical utilization of this fuel within engines be pursued, a preemptive measure of acidification or dilution becomes imperative. In terms of mitigating CO levels, an alternative approach could involve the elevation of the air proportion within the combustion process. In essence, the exploration of strategies to reduce CO emissions warrants careful consideration of the intricate balance between achieving optimal combustion efficiency and preserving the longevity of engine components. The NO_x concentration within diesel engine exhaust typically falls within the bracket of 50-1000 ppm. As demonstrated in Fig. 14, diesel fuel aligns with this range. Upon subjecting the engine to tests employing plastic waste-derived fuel, the NO_x levels distinctly remained below the stipulated threshold. However, the utilization of fuel derived from plastic waste notably curtails the interaction between nitrogen and other chemical constituents.

In general, nitric oxide (NO) originates through the amalgamation of nitrogen and oxygen at elevated temperatures and pressures, culminating in a colorless, odorless gas. This occurrence is characteristic of both the combustion process and the immediate aftermath of combustion. This observation implies that fuel derived from plastic waste, replete with the chemical compositions of benzene and acid groups, substantially diminishes the formation of NO_x during the diesel engine's combustion process. In essence, the fuel sourced from plastic waste, laden with its distinct chemical makeup, contributes to a noteworthy reduction in the creation of NO_x during the combustion sequences executed within diesel engines.

Fig. 14 provides an evident illustration that the NO_x levels emanating from engines fueled by natural catalytic sources stand beneath those generated by synthetic catalysts. Specifically, the utilization of HDPE-derived fuel yields a remarkable reduction in NO_x content, reaching levels as minimal as 8.1 ppm. This outcome intimates that the amalgamation of the benzene chemical composition within

this fuel serves to abridge the duration of combustion and lower the associated temperatures within the engine.^[19] Consequently, this dynamic engenders a scenario where the engine emits a diminished quantity of NO_x into the surrounding atmosphere. In essence, the incorporation of benzene within the fuel exhibits a distinct propensity to curtail both the temporal and thermal aspects of combustion, thereby contributing to the reduction in NO_x emissions during the engine's operational processes.

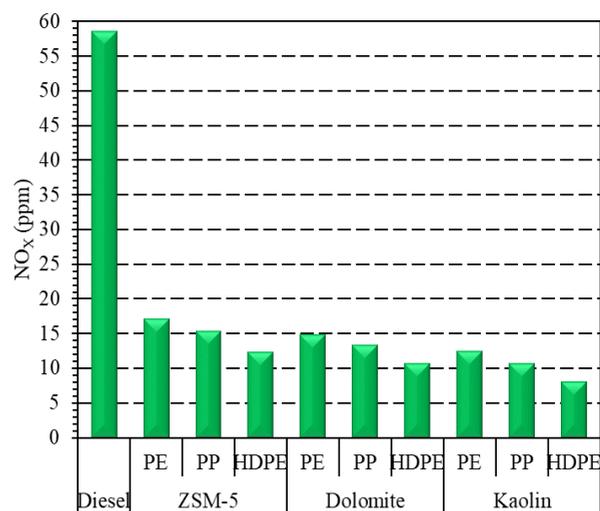


Fig. 14 NO_x emissions.

4. Conclusions

The production of fuel for diesel engines is derived through catalytic pyrolysis of plastic waste. The reaction transpires at a temperature of 500°C, and the catalysts, namely ZSM-5, dolomite, and kaolin, are also operated under the same temperature regimen. The research employs three distinct types of plastic waste, namely PE, PP, and HDPE. The findings underscore the capacity of natural catalysts to yield a greater fuel volume compared to synthetic counterparts. The kaolin catalyst, for instance, can generate fuel weighing up to 60.4 wt% when PE is employed as the raw material.

An investigation into fuel attributes reveals that the synthetic catalyst ZSM-5 can enhance the calorific value of PE-derived fuel to 42.2 MJ/kg. Conversely, fuel resulting from plastic waste pyrolysis using natural catalysts exhibits a diminished calorific value, attributable to the heightened presence of chemical constituents within the benzene group of the fuel. Consequently, pyrolysis of waste plastic fuel using natural catalysts engenders reduced braking horsepower and heightened fuel consumption.

Notably, pyrolyzed plastic waste fuel, facilitated by natural catalysts, demonstrates superior efficacy in mitigating air pollution originating from engine exhaust compared to plastic waste fuel pyrolyzed using synthetic catalysts. Furthermore, the kaolin catalyst imparts favorable attributes to the fuel, culminating in reduced CO and NO_x emissions when utilized within the engine.

In summation, it can be inferred that the employment of

natural catalysts for pyrolysis of plastic waste yields a larger fuel yield in comparison to synthetic catalysts. This produced fuel also contributes to a reduction in engine exhaust emissions, albeit at the expense of a potential reduction in engine horsepower, more pronounced than fuel obtained through synthetic catalyst-assisted pyrolysis. The prospect of enhancing this fuel involves the reduction of chemical constituents within the benzene and acid groups, a measure that could potentially bridge the quality gap between fuels obtained via pyrolysis using natural versus synthetic catalysts. Consequently, this research exhibits promise for further application and exploration.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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