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## Recovery of Waste Engine Oil by Pyrolysis Distillation Process

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**Abstract.** The aim of this research is to study the feasibility of recovering waste engine oil (WEO) into diesel-like fuel using a novel two-stage reactor. The system increases the oil yield and quality, representing a considerable progress in hazardous waste management. The study examines optimal process conditions, including pyrolysis and distillation temperatures, carrier gas flow rates, and the effects of three catalysts: Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and bentonite. The results show that the temperature directly affects the pyrolysis process, with thermal cracking being the main reaction. Increasing the carrier gas flow rate improves the heat transfer capacity of the feed oil, thereby enhancing oil breakdown in the reaction. The optimal conditions for producing pyrolysis oil were determined as a pyrolysis temperature of 400°C, a distillation temperature of 250°C, and a carrier gas flow rate of 30 mL/min. Under these conditions, the produced pyrolysis oil had the highest combined composition of naphtha, kerosene, and gas oil, with its specific gravity and viscosity falling within the diesel standards range, although the flash point remained below the standards. Under the examined catalysts, Na<sub>2</sub>CO<sub>3</sub> preferentially reacted with large hydrocarbon molecules, resulting in pyrolysis oil with heavy oil content. The use of Fe<sub>2</sub>O<sub>3</sub> significantly reduced the sulfur content in the oil, while bentonite had a greater selectivity for naphtha. The study particularly shows the integration of re-distillation as an additional refining step, which has successfully improved the flash point to meet diesel fuel standards. These results demonstrate the potential of this approach to recycle hazardous waste into valuable fuel products.

**Keywords:** Waste engine oil, catalytic pyrolysis, diesel-like fuel properties, hazardous waste management.

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## 1. Introduction

Waste engine oil (WEO) is the decomposed lubricating oil found in automobile engines, and its quantity has been increasing due to the rise in gasoline-powered vehicles. WEO is classified as hazardous waste, and its proper disposal is important to comply with the environmental regulations. Previous studies have shown that WEO contains heavy metals, phenols, and aromatic hydrocarbons, that represent the serious health risks [1, 2]. Therefore, researching effective management strategies and recycling methods to convert waste into valuable products is crucial. WEO consists of two main components. The first component contains valuable elements that can be recycled into a diesel-like fuel, known as base oil. This petroleum product is obtained through crude oil distillation and includes both aliphatic and aromatic hydrocarbons. The second component consists of additives necessary for improving the oil properties in vehicle engines, such as zinc dialkyl dithiophosphates (ZDDP), bisphenol, aromatic amine, silicone polymer, and other surfactants. The presence of these additives raises environmental concerns and requires their removal during the recycling process to produce high-quality fuel with minimal environmental impacts. Various techniques have been developed in recent years for recycling WEO. Two basic approaches include solvent extraction and adsorption to remove particles or undesired compounds. The solvent extraction separates undesirable substances from the waste by using their different solubilities in two immiscible liquids. On the other hand, the adsorption method employs solid adsorbents, such as natural clay, acidic clay, and carbon black to separate undesirable substances from the base oil. Both methods are considered physical separation processes that do not involve chemical reactions [3, 4, 5]. Despite their simplicity, these methods have disadvantages, including the release of toxic waste and the generation of additional waste that requires treatment. However, pyrolysis is a more promising approach that has attracted the attention of many researchers. Pyrolysis is a versatile thermal decomposition process that uses heat in an oxygen-free atmosphere to convert hydrocarbon compounds or organic materials into valuable products. Most energy research focuses on the pyrolysis of biomass to produce energy-efficient products for sustainable energy application [6, 7]. However, pyrolysis can also be applied to the conversion of WEO into diesel-like fuel, providing a promising route for waste utilization and energy recovery. During the pyrolysis process, thermal cracking reactions take place under controlled temperatures, breaking down hydrocarbon compounds and producing multiphase products such as pyrolysis oil, gases, and carbonaceous residues. The yield of these products varies significantly based on factors such as temperature and residence time. In addition, the conditions during pyrolysis affect the composition of hydrocarbon compounds, including aliphatic and aromatic hydrocarbons in pyrolysis oil, which leads to significant

changes in the diesel-like fuel properties [8]. It is important to develop the process for controlling these conditions to meet commercial oil standards. Some studies suggest that integrating a distillation unit to the process can improve the quality of pyrolysis oil [9, 10, 11]. Moreover, catalytic pyrolysis involves the strategic use of catalysts to facilitate the thermal breakdown of organic materials, such as waste oil, into smaller, more valuable molecules. This process is an advanced version of traditional pyrolysis, enhancing the efficiency of the process and improving the quality of the products. It offers several advantages such as an increase in reaction rate due to lower activation energy [12]. Different types of catalysts were used to improve the cracking process of waste engine oil, including bentonite clay [13, 14],  $\text{Na}_2\text{CO}_3$ ,  $\text{Fe}_2\text{O}_3$  [15], and  $\text{Fe}_3\text{O}_4$  [16].

This research presents a novel two-stage pyrolysis distillation reactor system, specifically designed with the second reactor functioning as a distillation column, which can enable precise temperature control during the distillation process in order to obtain oil products with the properties closer to the commercial standards. The optimal conditions in pyrolysis distillation process, including pyrolysis temperature, distillation temperature and residence time were investigated. The use of  $\text{Fe}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ , and bentonite catalysts is expected to improve the hydrocarbon composition and reduce the sulfur content, which may potentially bring the resulting oil closer to diesel fuel standards. Quantitative and qualitative analyzes of multiphase products follow the ASTM D 975 standard, including measurements of specific gravity, viscosity, flash point and sulfur content. Additionally, the integration of re-distillation as an additional refining step aims to address challenges such as low flash point. The expected outcome is that pyrolysis oil could be serve as a viable replacement for diesel oil in automotive applications.

## 2. Materials and Methods

### 2.1. Chemical and Reagents

WEO obtained from an automobile service center in Chon Buri, Thailand was used in this study without undergoing any pretreatment. Three types of catalysts were used: sodium carbonate ( $\text{Na}_2\text{CO}_3$ , 98%, ALFA AESAR), iron carbonate ( $\text{Fe}_2\text{CO}_3$ , 98%, ALFA AESAR) and sodium bentonite (commercial grade). Prior to use, all catalysts were pretreated in a tube furnace at 700 °C under a nitrogen atmosphere to remove impurities.  $\text{Na}_2\text{CO}_3$  plays an important role in increasing the yield of pyrolysis oil and improving its flash point [17].  $\text{Fe}_2\text{CO}_3$  is known for its effectiveness in reducing the sulfur content of the resulting oil [18]. Bentonite also helps to minimize the formation of coke during the pyrolysis process [19], which improves the overall efficiency of the reaction.

### 2.2. Pyrolysis Distillation Process of WEO

The two-stage reactor used in this study for the pyrolysis distillation process is depicted in Fig. 1. In a

typical operation, WEO was fed into the pyrolysis reactor, which was installed in the furnace. The reactor was gradually heated from room temperature to the target temperature under a nitrogen flow. The vapors were driven in the glass bead-containing distillation reactor and subsequently condensed as they passed through two cooling units: a condenser with a double-tube heat exchanger and a product cooler with a coil and shell heat exchanger. The produced pyrolysis oil was then collected in the product vessel.

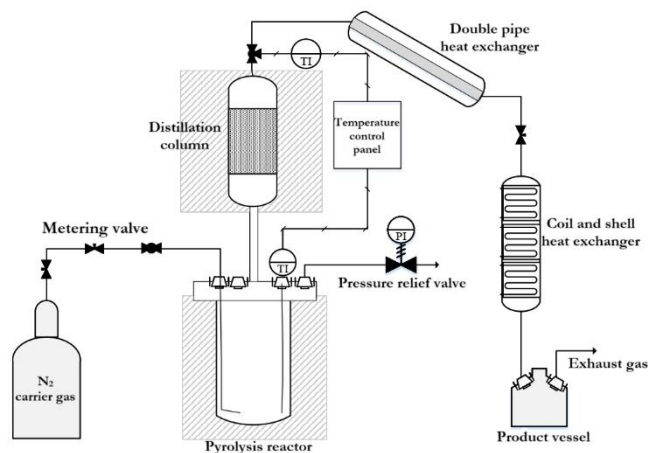


Fig. 1. Schematic of two-stage reactor for pyrolysis distillation process.

### 2.3. Preliminary Study

The preliminary study aims to determine the optimal temperature range for the pyrolysis process. Initially, 200 mL of WEO was introduced into the pyrolysis reactor and heated from room temperature to the desired temperatures at a heating rate of 5 °C/min, with a nitrogen flow of 10 mL/min. The distillation reactor was maintained at the same temperature. The process comprised six steps, starting with an initiation step at 200 °C, with a hold time of one hour. The experiment was then repeated at intervals of 50 °C and covered the temperatures from 250 °C to 500 °C. Pyrolysis oil produced at each temperature step was collected and weighed to determine the yield. All pyrolysis oil samples were subsequently analyzed on component identification using gas chromatography-mass spectrometry (GC-MS).

### 2.4. Study of Factors Affecting the Pyrolysis Process

The effects of various factors on the yield, composition, and properties of pyrolysis oil were investigated, including pyrolysis temperature, carrier gas flow rate, distillation reactor temperature, and catalyst type. Based on the results of the preliminary study, the pyrolysis temperature was varied in the range of 380 - 420 °C. The flow rate of the nitrogen carrier gas was set between 15 and 100 mL/min, while the temperature of the distillation reactor was varied between 250 and 350 °C, which corresponds to the boiling point range of automotive gas

oil obtained from crude oil distillation, typically used in vehicle engines. In order to evaluate the influence of catalyst type, 3 wt% of each catalyst, namely Na<sub>2</sub>CO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and bentonite, was added into 200 mL of WEO and the mixture was stirred for 1 hour before starting the process. The pyrolysis process for each condition was stopped after a 2-hour hold time at the specified temperature and the resulting pyrolysis oil was collected. The pyrolysis oil yield was defined as a percentage of the liquid weight collected in the product vessel relative to the total weight of the WEO, whereas the residue yield was calculated as a percentage of the remaining substance weight relative to the total weight of the WEO. The gas yield was determined from the difference between these values.

### 2.5. WEO and Oil Product Analysis

The properties of WEO and pyrolysis oil, such as viscosity, flash point, and sulfur content, were determined in accordance with ASTM standards. The kinematic viscosity was measured using a Tamson TV2000 viscometer bath in accordance with ASTM D 445. The determination of the flash point was carried out using a Pensky-Martens closed cup tester (NPM221, Normalab) in accordance with ASTM D93 guidelines. The sulfur content analysis was performed with an X-ray fluorescence spectrometer (XRF) using a Lab-X3500, Oxford instrument, following ASTM D4294 procedure. The composition of the pyrolysis oils of all conditions was analyzed by gas chromatography-mass spectrometry (Agilent 6890 GC-MS) equipped with a DB-5MS column, and the area fraction of the main components was determined.

## 3. Results and Discussion

### 3.1. Preliminary Study Results

The influence of the heating temperature on the pyrolysis oil yield was studied using a two-stage reactor to determine the optimal temperature that results in optimal yield and the preferred quality of the oil product. The temperature of the two-stage reactor both in the pyrolysis reactor as well as in the distillation reactor was incrementally varied from room temperature up to 200, 250, 300, 350, 400, 450, and 500 °C, with a holding time of one hour in each region. The yield of pyrolysis oil was calculated as shown in Fig. 2. The results show a slight increase in pyrolysis oil yield from 200 °C to 400 °C, with the highest yield observed at 450 °C and a significant decrease of more than half occurring at 500 °C. According to the thermal behavior of WEO analyzed by thermogravimetric analysis (TGA), the highest weight loss occurring between 400°C and 500°C [20]. This suggests that within this temperature range, WEO undergoes the most significant thermal decomposition into gaseous products, which subsequently condense into the maximum amount of pyrolysis oil.

While the pyrolysis oil yield is a screening factor to determine the optimal temperature, a GC-MS analysis is required to identify chemical components. Therefore, the

pyrolysis oils obtained at temperatures of 400 °C, 450 °C, and 500 °C were analyzed. The results are listed in Table 1. The area fraction of the oil components was identified based on the carbon number of the commercial oils specified by Coker [21]. The analysis result shows that the high temperature has an impact on the oil components, with the proportion of light hydrocarbons such as gasoline (C5-C11) increasing at 450°C and 500°C compared to 400°C. With increasing temperature, however, the proportion of kerosene and gas oil (C12-C19) as well as lubricating oil (C20-C27) decreased slightly. Since it depends on the nature of the thermal cleavage reaction, high energy is preferred for the cleavage of chemical bonds. Although long-chain hydrocarbons were heavily broken down into lighter hydrocarbons at higher temperatures, sulfur, and aromatic compounds also increased. In particular, the sulfur content has increased to more than double, which is concerning for diesel fuel standards. This can be attributed to the fact that some long chain hydrocarbons are complex molecules that contain sulfur and aromatic compounds that would be released from the molecules upon cracking. The results of this study are consistent with previous research by Yaqoob et al. [22], which observed similar trends in the increase in light hydrocarbon production at higher pyrolysis temperatures. Similarly, Oufkir, Zerraf and Belaouad [23] found that elevated temperatures in pyrolysis processes lead to higher yields of lighter hydrocarbon fractions but also increase the presence of undesirable sulfur compounds. Therefore, temperatures of 450 °C and 500 °C were not interesting for the production of diesel-like fuel from WEO, with 400 °C identified as the optimal temperature for further investigation.

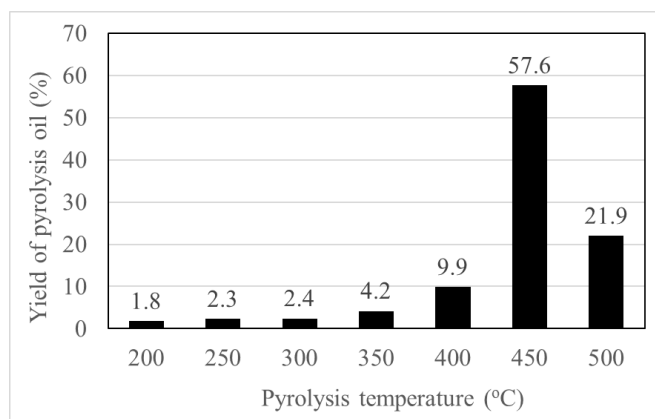


Fig. 2. Yield of pyrolysis oil varied with heating temperature.

Table 1. Pyrolysis oil components by distillation range.

Distillation range	Carbon number	Percentage		
		400 °C	450 °C	500 °C
Gasoline	C5-C11	30.2	28.3	37.2
Kerosene and gas oil	C12-C19	48.1	44.0	41.2
Lubricating oil	C20-C27	12.1	6.4	5.1
Heavy oil	>C28	0	0.0	2.2
Sulfur	-	3.0	6.4	6.2
Aromatic	-	5.2	2.8	6.1

### 3.2. Effect of Pyrolysis Temperature

The effect of the pyrolysis temperature on thermal cracking activity was studied at 400 °C, with the lower and upper temperatures limits set at 380 °C and 420 °C, respectively. The initial carrier gas flow rate was set to 30 mL/min and the distillation temperature of the second reactor was maintained at 250 °C. Multiphase products were obtained and converted into yield percentages, as shown in Fig. 3. The results indicate significant changes in the product phases with increasing temperature. The highest yield of pyrolysis oil and the lowest solid residues as char were achieved at 420 °C, the highest temperature in this experiment, because the thermal cracking reactions favor higher temperatures due to the endothermic nature. These findings are consistent with related research on carbon-hydrogen-based waste pyrolysis for diesel-like oil production. For example, Deepa et al. [24] investigated the pyrolysis of high-density polyethylene (HDPE) and polypropylene (PP) plastic waste blends. Their study found that as the pyrolysis temperature increased, the yield of pyrolysis oil also increased, reaching its peak at 450°C. Similarly, Faisal et al. [25] studied the optimization of oil yield in the pyrolysis of mixed plastic waste and reported the consistent results, demonstrating that pyrolysis oil yield generally increases with increasing pyrolysis temperatures. However, in addition to the product yield, optimal conditions should also be determined based on other factors such as oil components and oil properties, as shown in Fig. 4 and Table 2, respectively.

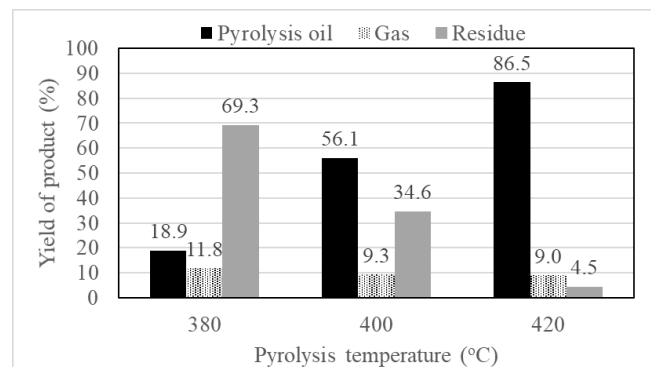


Fig. 3. Yield of products obtained from variations in pyrolysis temperatures.

The oil components shown in Fig. 4 were analyzed using distillation gas chromatography (DGC), with temperature limits defined according to the distillation ranges of crude oil, including, 88–193 °C for naphtha, 193–271 °C for kerosene, 271–343 °C for atmospheric gas oil (AGO), and above 343 °C for heavy oil [16]. The result show that the heavy oil content reached its maximum at 73.2% at 420°C and tended to decrease at lower temperatures, while lighter fractions such as naphtha, kerosene, and AGO obviously increased. However, the high pyrolysis temperature of 420 °C affected the oil viscosity, as shown in Table 2. The viscosity of heavy oil obtained at this temperature exceeded the standards

viscosity requirements for diesel fuel. Although the specific gravity of the pyrolysis oil was in an acceptable range, the flash point was below the standards, and the sulfur content exceeded regulatory limits. The low flash point may be attributed to the presence of volatile organic compound impurities, such as light oil and aromatics detected by GC-MS and DGC, as shown in Table 1 and Fig. 4. In addition, the sulfur content decreased from 0.42 wt% to 0.27 wt% as the pyrolysis temperature increased, however, it remained above the diesel fuel standards. The initial sulfur content in raw WEO was 0.45 wt%. These results indicate that sulfur removal via pyrolysis is limited, requiring additional desulfurization process to meet fuel quality standards.

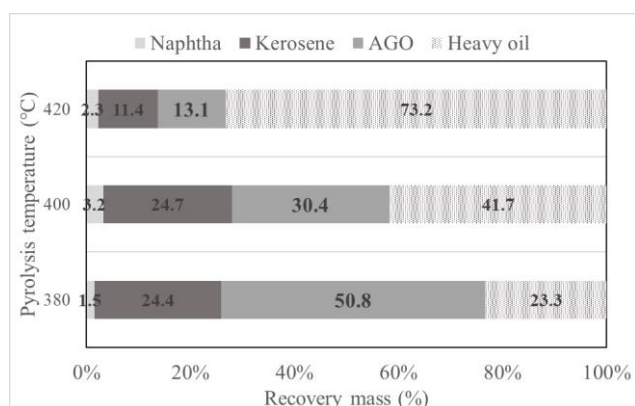


Fig. 4. Pyrolysis oil components for each pyrolysis temperatures.

Table 2. Properties of pyrolysis oil obtained from variations in pyrolysis temperatures

Properties	Pyrolysis temperature (°C)			WEO	Diesel standards <sup>a</sup>
	380	400	420		
Specific gravity	0.81	0.82	0.83	0.86	0.81-0.87
Viscosity (cSt)	1.6	2.6	5.9	63.7	1.8-4.0
Flash point (°C)	17	15	16	110	>52
Sulfur content (wt%)	0.42	0.28	0.27	0.45	<0.005

<sup>a</sup> Diesel fuel standards announced by the Department of Energy Business, Thailand.

As mentioned above, the study on the effect of pyrolysis temperature showed that a high temperature (420 °C) resulted in the largest oil yield. However, the viscosity exceeded diesel fuel standards, while the flash point and the sulfur content remained below acceptable limits under all conditions. Although some properties did not meet the required standards, a pyrolysis temperature of 400 °C appeared to be the optimal condition. Further investigations will be conducted to evaluate additional influencing factors.

### 3.3. Effect of Carrier Gas Flowrate

The variations in the carrier gas flow rate altered the residence time of the oil vapor in the pyrolysis reactor,

subsequently affecting the product yield and properties. At carrier gas flow rates of 15, 30, 50, and 100 mL/min, the corresponding residence times were 34.6, 17.3, 10.4, and 5.2 minutes, respectively. While studying the effect of carrier gas flow, the pyrolysis temperature was maintained to 400 °C and the distillation temperature in the second reactor was to 250 °C. The results are shown in Fig. 5. Product yields increased slightly with higher flow rates, reaching a maximum of 69% at 100 mL/min. A higher flow rate enhances the transport of volatile compounds, facilitating better separation and collection of pyrolysis products. This is because an increased flow rate helps flush gases more effectively, reducing the likelihood of secondary reactions that could otherwise lower the oil yield [26].

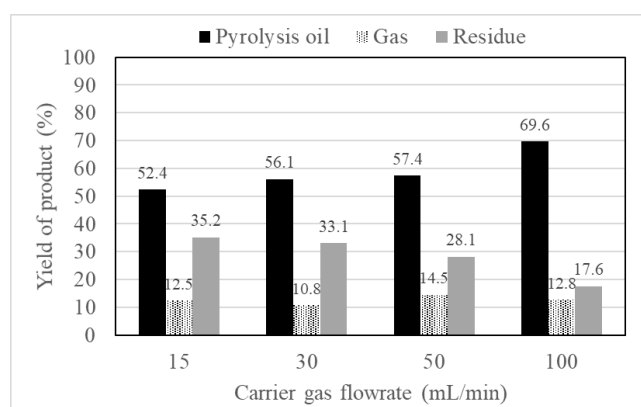


Fig. 5. Yield of products obtained from variations in carrier gas flowrate.

The analysis of pyrolysis oil properties, presented in Tables 3, reveals that the specific gravity of the oil meets the diesel fuel standards under all conditions. Regarding viscosity, only the carrier gas flow rate conditions of 30 and 50 mL/min produced oil with a viscosity of 2.6 cSt, which falls within the acceptable range for diesel fuel. The sulfur content of the oil is 0.29, 0.28, 0.28, and 0.27 wt% at carrier gas flow rates of 15, 30, 50, and 100 mL/min, respectively. While these values exceed diesel fuel standards, they are lower than the sulfur content of original WEO (0.45 wt%). This indicates that the pyrolysis distillation process can reduce the sulfur content to some extent, though high molecular weight sulfur compounds with high boiling points remain. This finding is consistent with a preliminary GC-MS analysis, which showed an increase in sulfur compound contamination in oil produced at temperatures between 450 and 500°C due to residue cracking. The carrier gas flow rate had no significant influence on the sulfur content. In addition, the flash point of pyrolysis oil was significantly lower than diesel fuel standards under all conditions due to the presence of light oil components such as naphtha, kerosene, and various volatile aromatic compounds. Quality analysis indicates that pyrolysis oil produced at flow rates of 30 and 50 mL/min is closest to diesel fuel standards. To determine optimal conditions for further experiments, the composition of the pyrolysis oil was analyzed using DGC, with the results shown in Fig. 6. It

was found that at a carrier gas flow rate of 100 mL/min, the heavy oil content was 66.2%, which is consistent with Fig. 5, showing a decrease in residue yield at this flow rate. Conversely, at a flow rate of 15 mL/min, the naphtha content was the highest at 10.0%, compared to the naphtha content of 3.2%, 9.3%, and 5.1% at flow rates of 30, 50, and 100 mL/min, respectively. This indicates that increasing residence time by reducing the carrier gas flow rate favors in the production of more short-chain hydrocarbon compounds. Conversely, decreasing residence time by increasing the carrier gas flow rate promotes the formation of long chain hydrocarbons.

When determining the optimal conditions by analyzing the proportions of naphtha, kerosene, and gas oil, it was found that a carrier gas flow rate of 30 mL/min resulted in the highest total content of these fractions (58.3%) compared to other flow rates. Considering both the quantity and quality of the pyrolysis oil, it is concluded that a flow rate of 30 mL/min is optimal. This condition was selected for further experiments to investigate the influence of the distillation temperature in the next section.

Table 3. Properties of pyrolysis oil obtained from variations in carrier gas flowrate.

Properties	Carrier gas flowrate (mL/min)			
	15	30	50	100
Specific gravity	0.81	0.82	0.81	0.82
Viscosity (cSt)	1.7	2.6	2.6	5.0
Flash point (°C)	16	15	18	20
Sulfur content (wt%)	0.29	0.28	0.28	0.27

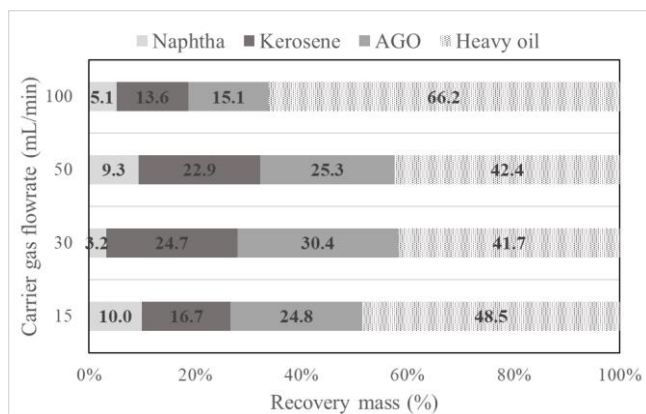


Fig. 6. Pyrolysis oil components for each carrier gas flowrate.

### 3.4. Effect of Distillation Temperature

The distillation temperature in the second reactor was varied between 250 °C and 350 °C to investigate its effect on the product yield and pyrolysis oil properties. The thermal cracking capability is reflected in the product yields, as shown in Fig. 7. The pyrolysis oil increased with rising distillation temperature from 300 °C to 350 °C, but no significant change was observed between 250°C and

300°C. At the highest distillation temperature of 350 °C, the vapor phase from the pyrolysis reactor could not condense efficiently in the distillation reactor and up to the cooling unit. On the other hand, at low temperature range (250–300 °C), condensation occurred more effectively, resulting in a lower pyrolysis oil yield a high proportion of residues from vapor condensation. Table 4 presents the qualitative analysis of pyrolysis oil, including specific gravity, viscosity, sulfur content, and flash point. The specific gravity of pyrolysis oil remained constant at 0.81 under all temperature conditions, which is in the diesel fuel standards. The viscosity values ranged between 2.6 and 3.5 cSt, meeting diesel fuel requirements. The sulfur content was measured at 0.28, 0.29, and 0.29 wt% at distillation temperatures of 250°C, 300°C, and 350°C, respectively. While these values exceed diesel fuel standards, they are lower than the sulfur content of the original WEO, indicating that the distillation temperature has no effect on the sulfur content. However, the flash point of pyrolysis oil remained below diesel fuel standards under all temperature conditions. This lower flash point was attributed to the presence of volatile substances, such as aromatic compounds and other light oils, as previously mentioned. The study shows that the distillation temperature did not affect the flash point because low flash point impurities remain in the pyrolysis oil.

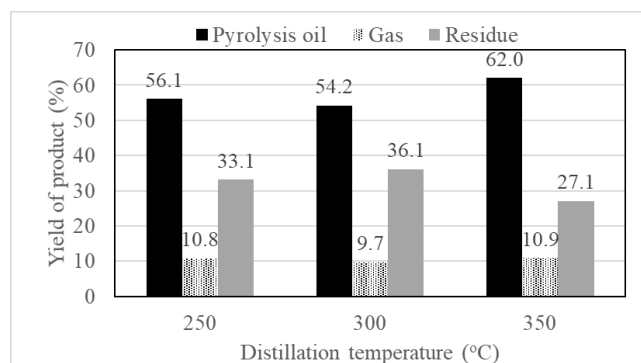


Fig. 7. Yield of products obtained from variations in distillation temperature.

Table 4. Properties of pyrolysis oil obtained from variations in distillation temperature.

Properties	Distillation temperature (°C)		
	250	300	350
Specific gravity	0.81	0.81	0.81
Viscosity (cSt)	2.6	2.7	3.5
Flash point (°C)	15	18	21
Sulfur content (wt%)	0.28	0.29	0.29

Using DGC analysis to determine the composition of pyrolysis oil based on the temperature cut points, and as shown in Fig. 8, it was found that at a distillation temperature of 250°C, the heavy oil content is 41.7%, the lowest compared to 48.6% and 57.3% at 300°C and 350°C, respectively. In terms of gas oil composition at 250°C, it was accounted for 30.4%, the highest compared to 23.6%

and 18.6% at 300°C and 350°C, respectively. Furthermore, the combined light components, including naphtha and kerosene, were highest at a distillation temperature of 250°C, reaching 27.9%. This aligns with the selection of 250°C as the distillation temperature, as it falls within the boiling range of gas oil in crude oil distillation.

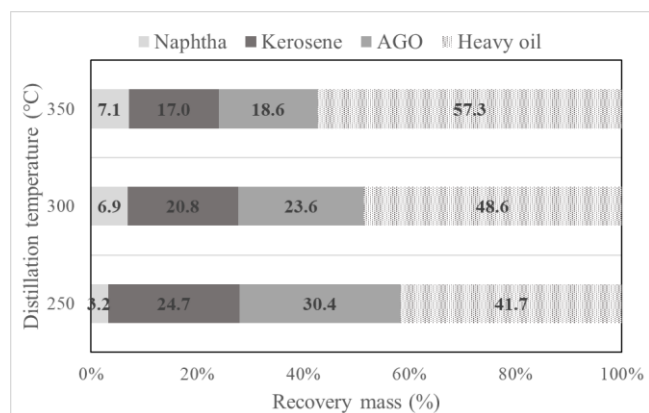


Fig. 8. Pyrolysis oil components for each distillation temperature.

The optimal conditions for the pyrolysis distillation process using a two-stage reactor system were determined based on the composition and properties of the pyrolysis oil. The study concludes that the appropriate pyrolysis temperature is 400°C, with a distillation temperature of 250°C and a carrier gas flow rate of 30 mL/min. These conditions will be applied in subsequent experiments to study the pyrolysis distillation process with catalyst addition in a two-stage reactor system.

### 3.5. Effect of Catalyst

An experiment was conducted to study the influence of catalysts in a two-stage reactor during the pyrolysis process. Catalysts such as  $\text{Na}_2\text{CO}_3$ ,  $\text{Fe}_2\text{O}_3$ , and bentonite were added at 3 wt% to enhance molecular cracking efficiency through catalytic cracking reactions in addition to thermal cracking reactions. The influence of these catalysts was investigated at a pyrolysis temperature of 400°C, a distillation column temperature of 250°C, and a carrier gas flow rate of 30 mL/min. Changes in product yield and quality, as well as the chemical composition of the pyrolysis oil, were analyzed. The percentage of product yields with and without catalysts are shown in Fig. 9.  $\text{Na}_2\text{CO}_3$  produced the highest pyrolysis oil yield of 58.9% and the lowest residue at 28.1%, while the gas yield was comparable to that of other catalysts. The conversion rate of the feedstock into oil and gas products using  $\text{Na}_2\text{CO}_3$  was also the highest at 71.8%. This indicates that  $\text{Na}_2\text{CO}_3$  effectively promotes catalytic cracking of large hydrocarbon molecules, resulting in increased oil and gas production. These results are consistent with those of Xu et al. [27] and Shie et al. [28], which reported that  $\text{Na}_2\text{CO}_3$  effectively facilitates the breakdown of oil sludge, which is mainly composed of large hydrocarbon molecules. Furthermore, Arpa, Yumrutas and Demirbas [10] and Demirbas et al. [17] observed that the addition of  $\text{Na}_2\text{CO}_3$

in the WEO pyrolysis results in oil products with a high proportion of long-chain hydrocarbons, as indicated by high boiling temperatures during distillation. This is likely due to the cracking of large molecules in the original oil, which aligns with the chemical composition analysis by GC-MS in Table 5. The heavy oil content ( $>\text{C}_{28}$ ) was 0.53% with  $\text{Na}_2\text{CO}_3$ , whereas no heavy oil was detected with other catalysts or non-catalyzed conditions. The residue content was higher when using  $\text{Fe}_2\text{O}_3$ . The  $\text{Fe}_2\text{O}_3$  catalyst resulted in a conversion rate of 67.9%, lower than  $\text{Na}_2\text{CO}_3$ , with a higher residue content, indicating less efficient catalytic cracking. However, GC-MS analysis showed that  $\text{Fe}_2\text{O}_3$  produced naphtha, kerosene, and gas oil compositions similar to those of  $\text{Na}_2\text{CO}_3$ .  $\text{Fe}_2\text{O}_3$  is widely used to produce light oil from high molecular weight hydrocarbons such as bitumen [29], oil sludge [18], and heavy oil [30]. Bhaskar et al. [9] also reported the use of  $\text{Fe}_2\text{O}_3$  to produce fuel oil from waste lubricating oil and found a significant reduction in sulfur content. This is consistent with Cheng et al. [18], demonstrating the effectiveness of  $\text{Fe}_2\text{O}_3$  in reducing sulfur through catalytic cracking. Conversely, bentonite resulted in the lowest feed oil conversion rate, with the lowest oil and gas yield and the highest residue content compared to other catalysts and non-catalyzed conditions. Bentonite may hinder catalytic cracking due to its oil-absorbing properties, which can absorb some long chain hydrocarbons [31]. Emam [32] reported that bentonite is used to improve oil quality by absorbing impurities, heavy metals, and dyes. Abdel-Jabbar, Zubaidy, and Mehrvar [33] pointed out the effectiveness of bentonite in reducing heavy metals in used lubricating oil. Its absorption of the original oil resulted in a higher content of light oil (naphtha C5-C11) (14.75%), which was greater than that observed with other catalysts or non-catalyzed conditions, thereby reducing the viscosity. This reduction in viscosity is consistent with findings by Kar [19], who reported a decrease in viscosity of pyrolysis oil when using bentonite for catalytic cracking.

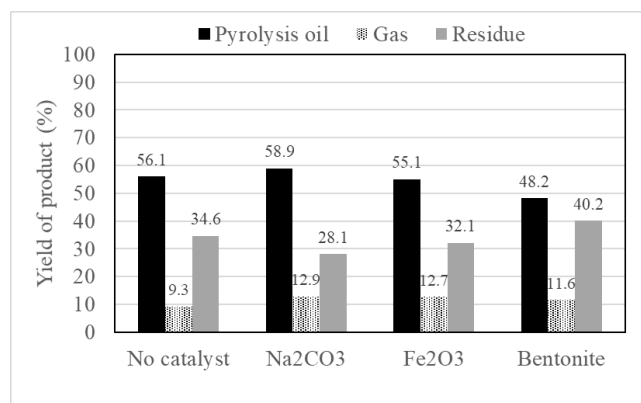


Fig. 9. Yield of products obtained from using different catalysts.

In addition to quantitative and chemical composition analysis of pyrolysis products, qualitative analysis is essential to evaluate the feasibility of using pyrolysis oil as a diesel substitute. The qualitative analysis of pyrolysis oil

from catalyzed and non-catalyzed pyrolysis at 400°C, compared to the diesel fuel standards is shown in Table 6. The specific gravity and viscosity of pyrolysis oil under all conditions ranged from 0.81-0.82 and 2.2-3.1 cSt, respectively, which is lower than used engine oil and within diesel fuel standards. Analysis of sulfur content revealed that catalyzed pyrolysis resulted in lower sulfur content than non-catalyzed pyrolysis, with Fe<sub>2</sub>O<sub>3</sub> achieving the greatest sulfur reduction to 0.22 wt%. Other catalysts and non-catalyzed conditions produced pyrolysis oil with a sulfur content of 0.26-0.28 wt%, attributed to the reaction of Fe<sub>2</sub>O<sub>3</sub> with sulfur during pyrolysis, forming Fe<sub>2</sub>O<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>, a super acid crucial for catalytic cracking [18]. However, the sulfur content in the pyrolysis oil did not meet diesel fuel standards (<0.005 wt%). Further study in desulfurization is necessary to achieve diesel quality.

The flash point of pyrolysis oil under catalyzed and non-catalyzed conditions ranged between 15-18°C, lower than the diesel fuel standards, indicating that the catalyst addition did not improve the flash point. Arpa et al. [8] and Phetyim and Pivsa-Art [34] reported that the low flash point of pyrolysis oil was due to the presence of volatile and flammable impurities, which were not effectively removed by the catalytic cracking. Re-distillation of the pyrolysis oil to remove these compounds significantly increased the flash point. Therefore, in this study, the pyrolysis oil produced under optimal conditions was re-distilled under the same conditions. It was found that the

flash point of the pyrolysis oil increased to 92°C, meeting the diesel fuel standards.

Table 5. Products classified by carbon number range at a temperature of 400°C.

Catalyst	Percentage of product			
	Naptha C5-C11	Kerosene and gasoil C12-C19	Lubricating oil C20-C27	Heavy oil >C28
No catalyst	12.63	62.26	14.60	0
Na <sub>2</sub> CO <sub>3</sub>	10.97	60.90	18.74	0.53
Fe <sub>2</sub> O <sub>3</sub>	11.61	60.46	19.03	0
Bentonite	14.75	61.73	13.83	0

Table 6. Properties of pyrolysis oil obtained from using different catalysts.

Properties	Type of catalyst			
	No catalyst	Na <sub>2</sub> CO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Bentonite
Specific gravity	0.82	0.82	0.81	0.81
Viscosity (cSt)	2.6	3.1	3.0	2.2
Flash point (°C)	15	18	15	15
Sulfur content (wt%)	0.28	0.26	0.22	0.27

Table 7. Comparison of pyrolysis oil properties from this study to the previous studies.

Sample name [ref]	Method	Specific gravity	Viscosity (cSt)	Flash point (°C)	Sulfur content (wt%)
WEO (this study)	two-stage reactor (without catalyst)	0.82	2.6	15	0.28
	two-stage reactor (with catalyst)	0.81-0.82	2.2-3.1	15-18	0.22-0.27
	two-stage reactor and re-distillation	0.82	2.6	92	0.28
Waste lubricating oil [5]	solvent extraction	0.90-0.91	7.05-10.3	195-200	N/A
	adsorption	0.89-0.90	9.8-11.1	225-238	N/A
WEO [10]	pyrolytic distillation (with CaO catalyst)	0.82	3.49	57	0.35
Waste lubricating oil [17]	pyrolytic distillation (with Na <sub>2</sub> CO <sub>3</sub> catalyst)	0.82	3.6	58	0.34
Used lubricant oil and mixed plastic waste [34]	co-pyrolysis	0.81-0.85	1.76-2.20	28-29.5	N/A
Waste automotive engine oil (WO) [35]	microwave-heated pyrolysis	0.76-0.77	6.2-6.9	<19	0.02-0.03

Table 7 summarizes the main properties, including specific gravity, viscosity, flash point, and sulfur content of the pyrolysis oil obtained in this study compared to previous research on various fuel oil recovery techniques. The pyrolysis oil from this study, particularly with Na<sub>2</sub>CO<sub>3</sub> catalyst and re-distillation, achieved properties close to diesel fuel standards, with a specific gravity of 0.82 and viscosity of 2.6 cSt. These values are within the acceptable

range for diesel applications, in contrast to oils from solvent extraction or adsorption processes, which exhibited higher viscosity (7.05–11.1 cSt) and specific gravity (0.89–0.91). The flash point of pyrolysis oil before re-distillation (15–18°C) was lower than that obtained using other methods but significantly improved to 92°C after re-distillation, meeting the diesel fuel standards. This highlights the importance of including re-distillation step



in this study, a process often overlooked in related research. Regarding sulfur content, the product oil in this study using  $\text{Na}_2\text{CO}_3$  reached valued of 0.22 wt%, which is lower than pyrolysis oils prepared with  $\text{CaO}$  (0.35 wt%) and  $\text{Na}_2\text{CO}_3$  (0.34 wt%) in previous studies. The microwave pyrolysis [33] achieved the lowest sulfur content (<0.03 wt%) due to the selective cracking facilitated by the microwave heating environment. These comparisons demonstrate the novelty of the two-stage reactor system in this study, which optimized both oil yield and quality. However, the results also highlight areas for further improvement, particularly in desulfurization processes, to achieve ultra-low sulfur diesel fuel standards.

#### 4. Conclusions

This research designed a two-stage reactor to study the feasibility of converting used engine oil into diesel-like fuel for reuse. The study focused on optimizing the conditions of the pyrolysis distillation process and evaluating the effects of catalysts, including  $\text{Na}_2\text{CO}_3$ ,  $\text{Fe}_2\text{O}_3$ , and bentonite on pyrolysis performance. The results indicate that increasing the pyrolysis temperature leads to a higher yield of pyrolysis oil. Likewise, increasing the temperature in the distillation column and the carrier gas flow rate result in higher oil yields. Considering the composition of the pyrolysis oil, the optimal conditions for pyrolysis distillation in this study were determined to be a pyrolysis temperature of 400°C, a distillation column temperature of 250°C, and a carrier gas flow rate of 30 mL/min. Under these conditions, the resulting pyrolysis oil had the highest combined composition of naphtha, kerosene, and gas oil, with viscosity and specific gravity falling within the standards range for diesel fuel, although its flash point remained below the standards. Among the catalysts used,  $\text{Na}_2\text{CO}_3$  provided the highest pyrolysis oil yield of 58.9% and the lowest residue content of 28.1%.  $\text{Na}_2\text{CO}_3$  exhibited the ability to selectively react with large hydrocarbon molecules, resulting in the presence of heavy oil in the pyrolysis oil.  $\text{Fe}_2\text{O}_3$  resulted in a lower oil yield than  $\text{Na}_2\text{CO}_3$  but resulted in the lowest sulfur content in the pyrolysis oil at 0.22 wt%. Bentonite provided the lowest oil yield compared to the other catalysts but exhibited the highest selectivity for naphtha (C5-C11). However, none of the catalysts increased the flash point of the pyrolysis oil. The study found that re-distillation the pyrolysis oil increased the flash point to 92°C, which meets the diesel fuel standards.

In terms of practical applications, the results underline the potential of this process to recycle hazardous waste engine oil into valuable diesel-like fuel for industrial use. The reduction of the sulfur content and the production of fuels with properties close to diesel fuel standards demonstrate both environmental and industrial significance. However, the fulfillment of stringent fuel standards requires additional refining steps, such as advanced desulfurization and impurity removal. Further studies should also focus on scaling up the process and

evaluating the performance of the fuel in practical applications.

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