

Catalytic Copyrolysis of Used Waste Plastic and Lubricating Oil Using Cu-Modification of a Spent Fluid Catalytic Cracking Catalyst for Diesel-like Fuel Production

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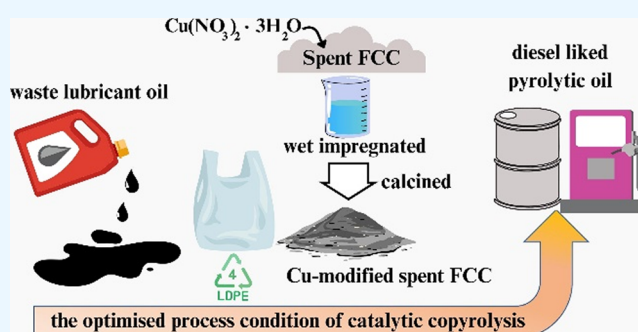
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ABSTRACT: This work provided catalytic copyrolysis of spent lubricating oil (SLO) with waste low-density polyethylene (LDPE) using copper modification of a spent fluid catalytic cracking (sFCC) catalyst to produce diesel-like fuels in a microbatch reactor, which will lead to effective waste management, ensure sustainability, and serve as an alternative energy source. The effects of LDPE blended with SLO, temperature, reaction time, and catalyst loading using an inert nitrogen atmosphere were investigated on the yields and distributions of copyrolyzed oil, while metal modification of the sFCC was prepared and used to investigate the catalytic activity. The temperature and time of reaction played an important role in the gaseous contribution to the pyrolysis of SLO. The addition of the LDPE ratio in the catalytic copyrolysis, including Cu loading on a spent FCC template, also enhanced the acidity and was responsible for the catalytic activity, which could improve the product distribution and chemical compounds in a range of diesel-like fuels. It was shown that the pyrolyzed oil was in the range of C_7 – C_{26} with a maximum diesel-like fraction of 23.11 ± 2.88 wt % compared with the catalytic pyrolysis of SLO alone, which contained a diesel-like fraction of only 12.45 ± 1.92 wt %. It was noticed that the acid active site of the catalyst resulted in a carbon–carbon bond cleavage and further secondary reaction, leading to the conversion of the long residue fraction into a light oil product. In addition, the LDPE ratio in the catalytic copyrolysis could improve the product distribution and chemical compounds in a range of diesel-like compounds, as confirmed by the GC/MS analysis. Catalytic copyrolysis oil of the optimal process condition (0.7:0.3 mass molar of SLO/LDPE, 450 °C, 60 min, 3 wt % Cu-sFCC, and 10 wt % catalyst loading) mainly contains light hydrocarbons in the C_7 – C_{19} range. Accordingly, both the product selectivity and the conversion of the long residue to the diesel-like fraction were nearly stable ($59.01 \pm 1.36\%$) during the catalyst reusability test from one to three cycles without regeneration and significantly decreased after the fifth cycle. This is an indication that the copyrolysis enhanced the conversion of SLO by LDPE blended into smaller hydrocarbon compounds, and the catalytic activity therefore showed a major tendency toward the formation of diesel-like fractions (C_8 – C_{18}).



1. INTRODUCTION

The rapid decrease in world energy resources coupled with an increase in energy and fuel consumption in accordance with rapid population and economic growth along with the growth of industry and service productivity has led to an increase in the level of traditional fossil fuels. At the same time, fossil fuel transformation and environmental concerns regarding carbon dioxide and greenhouse gas emissions from the burning of fossil fuels have led to increased attendance for research on renewable energy, which plays a role in candidate super clean fuel production and sustainable energy for future energy supply, which could reduce the energy demand of fossil fuels. Spent lubricating oil (SLO) is a waste product that usually occurs when oil is used to lubricate a mechanical part in the engine of vehicles and machinery. During use, a lubricant generally undergoes chemical changes, and its properties change due to oxidation in air, moisture, high temperature, and

contamination with others, causing the performance to deteriorate until it ceases to meet the lubricated quality that needs to be replaced,^{1,2} which causes the waste lubricating oil to be discharged in large quantities waste every year. Therefore, SLO, also composed of heavy metals, polyaromatic hydrocarbons, and chlorinated polycyclic aromatic hydrocarbon compounds, is classified as hazardous waste because it is highly toxic and a potentially carcinogenic substance that has a serious impact on human health, irritating, and corrosive

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properties that lack proper disposal, resulting in pollutant contamination and environmental impact.

The thermal and catalytic conversion of SLO into fuels is an alternative way of converting waste into valuable fuel oil to enhance the value of waste and manage those pollutants through appropriate processes to preserve the environment. Along these lines, the conversion of SLO into alternative fuel has raised concerns about its impact and accumulation in the environment.

Generally, SLO is heated in the absence of oxygen or an inert gas atmosphere and thermally cracked, and large hydrocarbon chains are randomly thermally decomposed into smaller hydrocarbons until the hydrocarbon chain is shortened to yield products that can be used as fuel oil.^{3,5,6,7} Unfortunately, some limitations of the random decomposition of SLO at high-temperature process condition may produce a large amount of smaller noncondensable gas, which requires control of the operation conditions.^{3,5,8} Alternatively, catalysts are used in the pyrolysis of SLO to obtain oil products with a large number of carbon atoms.

Noble metal acid catalysts are highly expensive and need regeneration after the reaction, while it is necessary to investigate an inexpensive alternative active catalyst that has a long lifetime and good catalytic performance for the production of pyrolysis oil from SLO.^{9–12} Therefore, many researchers have also focused on the product distribution and further treatment to improve the physicochemical properties and fuel quality,^{8,9,11,13,14} including the copyrolysis of feedstocks with high H/C material, such as waste polymer and less oxygenate composition.^{3,14–21} Low-density polyethylene (LDPE) can be co-fed with SLO, enhancing the role of LDPE and its synergy of both thermal decomposition and further catalytic reaction, resulting in shortened hydrocarbon molecules and conversion into desirable pyrolysis oils when compared with the pyrolysis oil obtained from the pyrolysis of individual SLO.^{14,22–24} Furthermore, upgrading the coprocessing of SLO and LDPE is also a candidate process with some acid/basic heterogeneous catalysts to produce a diesel-like grade. In general, zeolites, especially fluid catalytic cracking catalysts (FCCs), are widely used as heterogeneous acid catalysts in oil refining industries^{9–11,15,17} due to their textural properties, microporosity, thermal stability and acidity, resulting in the conversion of crude oil into commercialized fuels and liquified petroleum gas.

The product distribution of hydrocarbons from the catalytic reaction consisted of several carbons ranging from C₁ to C₄ gaseous products, naphtha, kerosene, gas oil, diesel and carbonaceous hydrocarbon compounds,²⁵ revealing mainly the process conditions and several types of catalysts employed with pore structures, surface areas and acid active sites of the catalysts.^{9,11,13,19,20,24}

In addition, the presence of micropores limits the catalytic performance for bulky molecules, especially for the hydroconversion of large hydrocarbon compounds to naphtha-like fuels.

However, one major limitation of microporous catalysts is often limiting the catalytic activity and further catalytic efficiency for a large hydrocarbon compound according to intracrystalline diffusion, resulting in obstacles to the cracking reaction, isomerization, and arrangement of large hydrocarbon molecules into smaller hydrocarbon compounds at similar fractions to naphtha kerosene or diesel.^{11–18,25} Consequently, the modification of zeolite with metal doping has attracted

much attention to improving both the acid strength and catalytic activity of the cracking reaction,^{26–28} which might favor a higher yield of shortened hydrocarbon compounds that also effectively improve the catalytic oil to meet the stringent standard properties for diesel-like products in commercialized transport fuels.^{15,17,24,28–30} Therefore, plastic waste entails dumping it at landfills, which can lead to numerous environmental pollution. The disposal of spent lubricant oil is collected and burned to produce heat energy, whose potential can be converted into energy by thermochemical reaction. This research illustrates that addressing these issues by recycling both plastic wastes and waste lubricating oil into fuels could contribute to the long-term management of waste. Both types of proper waste management are realized as effective sources of cheap raw materials to produce more affordable sustainable fuels than expensive refined crude oils. Furthermore, this copyrolysis of plastic waste and spent lubricant oil also promotes the upcycling of deteriorated materials as classified to waste materials into useful products while simultaneously reducing the amount of waste materials that pollute the environment according to adopt a concept of circular economy and line in a sustainable development goal.

This research aims to understand the optimal process conditions of catalytic copyrolysis of SLO and LDPE blended to diesel-like oil production. The effect of temperature, reaction time, and the mass molar ratio of LDPE blended to SLO, using the different mass molar of Cu impregnated into the sFCC catalyst, and the percentage of catalyst loading on the desirable diesel-like product yields and quality were also investigated to explain that thermal degradation of plastics waste into hydrogen radical and hydrocarbon radical promotes the carbon–carbon bond cleavage of large hydrocarbon chains from SLO. Meanwhile, the catalytic copyrolysis enhances the bond cleavage of plastic waste, which easily disintegrates, and promotes the hydrogenation reaction enhancing the carbon–carbon bond cleavage of SLO, then shape selective at the textural structure of the catalyst produced both LDPE and SLO into small straight-chain hydrocarbon product. Additionally, the physicochemical properties of pyrolyzed oil investigated under optimum conditions were characterized to determine the optimal process conditions to produce diesel-like oil while adhering to the circular economy concept. The stability of the catalyst was determined in terms of the reusability of the Cu-modified FCC catalyst in the copyrolysis of SLO and LDPE under the optimal conditions to obtain the desirable yield of diesel-like oil when compared with the noncatalytic pyrolysis of SLO alone.

2. MATERIALS AND METHODS

2.1. Feedstock. SLO collected in the form of waste motor oil by several motor garages in Bangkok, Thailand, was collected in airtight bottles, and then the air inside the bottle was purged with nitrogen gas to prevent oxidation of SLO with oxygen and stored until the test. LDPE plastic waste was collected and sorted from a municipal landfill in Saraburi Province, Thailand, first cut by a high-speed plastic cutting machine and then sorted into a size distribution of approximately 0.5 × 0.5 cm. The tests in the proximate and ultimate analyses of the SLO and LDPE were performed in accordance with ASTM D 7582-10. A CHN-628 CHN analyzer (LECO Corp., U.S.A.) was carried out to determine the elemental analyses of carbon, hydrogen, nitrogen, and

sulfur, whereas the oxygen content was also determined according to the different analysis percentages.

2.2. Catalyst Preparation and Characterization. The spent FCC (Star Petroleum, Rayong, Thailand) was used as a catalyst compared with the modification of metal loading into the spent FCC template. A copper-modified sFCC was prepared by using the wet impregnation method by varying several mass percentages of Cu (1–5 wt %) in the sFCC template. A total of 4.00 g of the spent FCC catalyst and a prescribed copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) were weighed and then dissolved in deionized water to a Cu concentration of a desirable wt % and continuously agitated with a magnetic stirrer at 600 rpm and 80 °C for 6 h. The slurry was filtered and washed using deionized water until the nitrate ions were completely washed out and then dried in a hot air oven at 120 °C for 24 h and calcined at 550 °C for 5 h. Then, the modified Cu-sFCC was reduced at 20 mL min⁻¹ flow rate in a hydrogen atmosphere at 400 °C for 2 h and subsequently under a low flow rate of 1%-vol O₂ atmosphere at room temperature for 18 h to reduce CuO-sFCC to metallic Cu-sFCC. The characterization of the catalyst samples was carried out using a D8 Advance X-ray diffractometer (Bruker Corp., Germany) at 40 kV and 40 mA with Cu K α radiation at λ of 1.5406 nm to determine the XRD pattern in the 2 θ range of 5°–85° at a 5° min⁻¹ scanning rate. An S8 Tiger X-ray fluorescence (XRF) spectrometer (Bruker Corp., Germany) was used to determine the mineralogical composition. An ASAP 2020 instrument (Micromeritics Instruments, U.S.A.) was used to determine the textural properties (surface area, pore volume, and pore size) by nitrogen adsorption–desorption isotherms conducted at 77 K.

2.3. Catalytic Pyrolysis Reaction. The test of catalytic copyrolysis of SLO and LDPE was conducted in a 70 mL custom-built stainless-steel cylindrical reactor. A pressure gauge and safety valve were used to monitor the occurrence of pressure change within the reactor during the pyrolysis reaction and relieve pressure in the system when it became too high. Figure 1 illustrates a schematic diagram for catalytic copyrolysis experiment. The reactor was assembled with an injection heating coil using a proportional integral derivative

(PID) temperature control unit and shaker to achieve thermal decomposition and maintain heat transfer throughout the reaction. In each test, approximately 20 g samples of SLO/LDPE mass molar blended with several ratios (1:0, 0.1:0.9, 0.3:0.7, 0.5:0.5, 0.2:0.8, and 0:1 SLO/LDPE), the weight percentage of copper impregnated to the sFCC catalyst (1 wt %, 3 wt %, 5 wt %, and no Cu loading), and catalyst mass molar loading to the sample (1 wt %, 5 wt %, 10 wt %, 20 wt %, and no catalyst) were performed in the experiment. Inert N₂ was supplied into the reactor to ensure the absence of an oxygen atmosphere, after which inert N₂ was fed into the reactor to attain 1 bar for all the tests at operating temperatures of 400, 425, 450, and 475 °C. Pyrolysis of individual SLOs was also performed at 450 °C for comparison.

The reactor was heated by an inductive heater from ambient temperature to the desired operating parameters and kept isothermal until the end of the pyrolysis reaction. The temperature was controlled by a PID with a K-type thermocouple detector, which was used to monitor the temperature inside the reactor. The catalytic pyrolysis reaction is isothermal due to the temperature being controlled by a PID electrical furnace. After completing the reaction, the reactor was immediately quenched into an ice bath to rapidly cool to the ambient temperature to avoid further cracking reactions and the formulation of solid carbonaceous inside the reactor,²⁵ while the noncondensable gas was kept in the reactor until the temperature inside a reactor was close to ambient temperature, then released through the gas drier unit before being collected in a gas bag to further determine the gas composition using a Shimadzu GC-2014 gas chromatograph (Shimadzu Corp. Japan) that were equipped with both flame ionization (FID) and temperature controlled detectors (TCD). Quantitative analysis using an external standard method was conducted to analyze the detected gases. A mass balance was performed to determine the yields of the solid, liquid, and gaseous products. The liquid oil was separated using vacuum filtration from the solid carbonaceous material and catalyst, while the gaseous yield was calculated in accordance with the mass balance from eqs 1–3:

$$Y_{\text{liquid}} = \frac{M_2}{M_1} \times 100 \quad (1)$$

$$Y_{\text{solid}} = \frac{M_3}{M_1} \times 100 \quad (2)$$

$$Y_{\text{gas}} = 100 - (Y_{\text{liquid}} + Y_{\text{solid}}) \quad (3)$$

where M_1 , M_2 , and M_3 represent the mass of the feedstock, the mass of pyrolytic oil, and the mass of only carbonaceous solid after the completed catalytic copyrolysis, respectively. Additionally, the small noncondensable gaseous yield was determined by the difference mass balance calculation. In this study, the test was performed in three replicates to illustrate the average product yield and product distribution, and the standard errors between the replicates under the same conditions were all below 5%.

2.4. Product Analysis. The sample liquid oil was collected and diluted with 1:100 carbon disulfide (Sigma–Aldrich, Singapore) and analyzed using a Varian CP-3800 (Varian Medical Systems, Inc., U.S.A.) simulated distillation gas chromatograph connected to an RTX2887 capillary column and FID detector in accordance with crude oil evaluation (ASTM method 2887-D86). Typically, the analysis of liquid

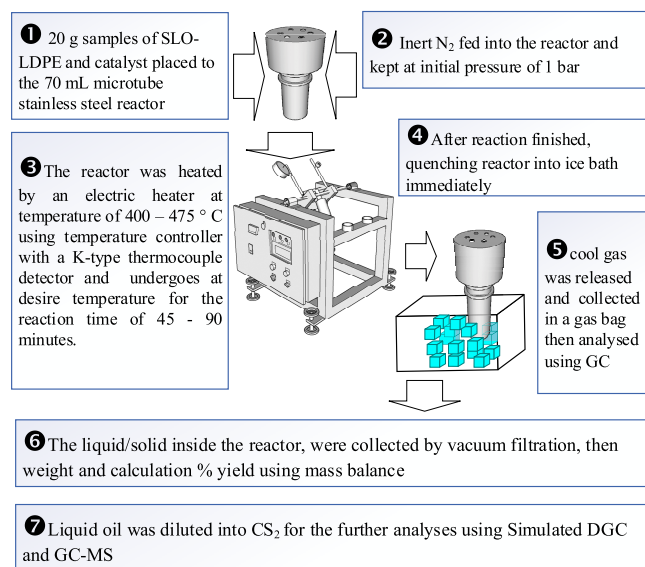


Figure 1. Schematic diagram for catalytic copyrolysis.

product distribution consisted of main fractions of naphtha-like (initial boiling point -220 °C), kerosene-like (221 – 250 °C), diesel-like (251 to 370 °C), and long residues (371 °C to final boiling point) represented in the product distribution.²⁵ Additionally, the sample pyrolysis oil was analyzed with gas chromatography/mass spectrometry (GC/MS) for qualitative analysis. Approximately 1 μL of the sample was injected into an Agilent 7890 gas chromatograph, a split/splitless injection unit, and an HP-5MS capillary column (30 m \times 0.25 mm \times 0.25 μm) equipped with an Agilent 5978 (Agilent Technologies, USA) coupled with a 5977A mass spectrometer. During the GC analysis of pyrolysis vapor products, the oven temperature was initiated from 50 to 200 °C and then to 350 °C with a heating rate of 10 °C min^{-1} and held for 10 min. The injector and MS detector temperatures were held at 280 °C. The mass spectrometer was operated in EI mode at 70 eV, and the mass spectra were obtained from m/z 50 – 5000 to investigate the chemical compounds. The chromatographic peaks were identified according to the NIST MS library and then calculated as a percentage of the total peak area. Additionally, the compounds present in the pyrolysis oil and their corresponding area % reveal molecular formulas that were presented.

A LECO CHN analyzer was used to determine the amounts of carbon, hydrogen, nitrogen, and sulfur in the elemental analysis of the obtained pyrolysis oil. Furthermore, the physicochemical analyses and fuel properties of liquid fuels were also determined. The kinematic viscosity was analyzed by using a HAAKE MARS iQ rheometer (Thermo Scientific, U.S.A.) at 40 °C in accordance with ASTM D445. The modification acid number (MAN) was determined using a Trinoplus 848 automated titration (Metrohm AG, Germany) in accordance with ASTM D66 due to the amount of KOH that neutralized the oil/solvent mixture. Additionally, a LECO AC-350 adiabatic bomb calorimeter was used to determine the higher heating values (HHV) in accordance with ASTM D240.

2.5. Catalyst Stability and Reusability. After the reaction finished, the pyrolyzer was rapidly cooled in an ice bath to ambient temperature; the spent catalyst and carbonaceous material were separated by using vacuum filtration, and the filtrated pyrolyzed oil and solid residue were collected. Both the spent catalyst and carbonaceous material were dried at approximately 105 °C in a hot air oven and then weighed. The carbonaceous material was determined by using the mass difference of the catalysts prior to the tests and then directly applied to the next catalytic reaction without any washing or regeneration. The reusability of spent FCC was determined by measuring the corresponding conversion of the long residue fraction into the diesel-like yield.

3. RESULTS AND DISCUSSION

3.1. Feedstock Characterization. Table 1 illustrates the proximate and elemental analyses of both SLO and LDPE plastic waste in accordance with the ASTM standard, including the HHV. The ultimate analysis of the SLO shows that the relative contents of C, H, O, and N are 79.55 , 12.59 , 7.72 , and 0.14 wt %, respectively. The amount of sulfur cannot be detected, causing neither very low sulfur nor no sulfur to be contained. The oxygen content in SLO is formed by oxidation by air during operation, which was found to be up to 7.72 wt %, and O/C shows a lower value of 0.07 , resulting in no significant changes in the HHV.

Table 1. Proximate and Ultimate Analyses

	SLO	LDPE waste plastic
proximate analysis ^a (wt %)		
volatile	82.13	94.57
ash	8.42	1.12
fixed carbon ^b	8.34	4.31
ultimate analysis (wt %)		
carbon	79.55	80.69
hydrogen	12.59	19.31
nitrogen	0.14	n.d.
oxygen ^b	7.72	n.d.
H/C (mol/mol)	1.90	2.87
O/C (mol/mol)	0.07	
HHV (MJ/kg)	41.65	49.88
kinematic viscosity (mm^2/s)	40.07	n.a.
MAN ($\text{mg}_{\text{KOH}}/\text{g}$)	5.31	n.a.

^aDry basis. ^bCalculation by the difference method. n.a. = not applicable, n.d. = not detected.

The analyses of LDPE consisted of 80.69 wt % carbon and 19.31 wt % hydrogen only. The proximate analysis shows that SLO consists of volatiles, fixed carbon, and ash at 82.13 , 8.34 , and 8.42 wt %, respectively. In addition, the raw SLO presents the relative contents of the composition according to the boiling temperature range using a simulated distillation gas chromatograph in the procedure of the ASTM 2887-D86 method, which consisted of naphtha-like (0.15 wt %), kerosene-like (3.11 wt %), diesel-like (7.67 wt %), and long residue (89.07 wt %). In contrast, LDPE is characterized using a CHN analyzer to investigate the content of carbon, hydrogen, and oxygen. The results represent the high H/C molar ratio because LDPE plastic waste is primarily composed of carbon, hydrogen, and an oxygen-free composition,¹⁵ while both nitrogen and sulfur are not detectable. Furthermore, the HHV analysis according to the adiabatic bomb calorimeter indicates that both raw feedstocks have higher calorific heating values.

The X-ray diffraction (XRD) analyses of the patterns of the new FCC catalyst, spent FCC catalyst, and Cu impregnated to sFCC catalysts are compared in Figure 2. The XRD patterns

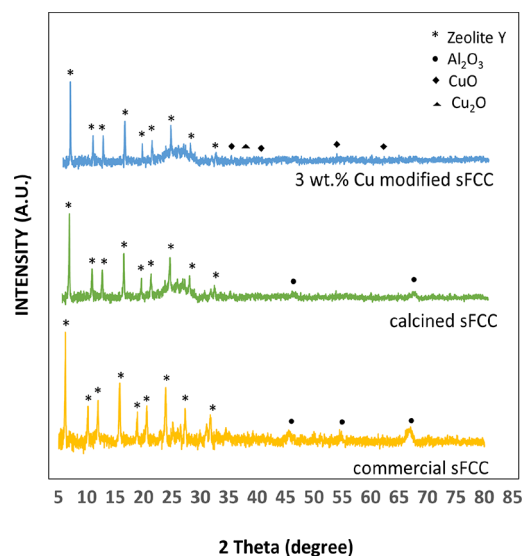


Figure 2. XRD pattern.

represent 2θ of 6.233, 10.160, 15.640, 23.636, 27.043, and 31.379, which matched the diffraction from indices of the (111), (220), (331), (533), (642), and (555) planes and are obviously detected in accord with the typical FCC catalyst of the γ -Al₂O₃ (zeolite Y) structure. When comparing the XRD patterns of Cu-modified sFCC with those of FCC and calcined sFCC catalysts, it is also difficult to find some obvious changes, and the modification of Cu on the sFCC parent template illustrates the XRD patterns of faujasite structures. Additionally, the modification of Cu to the sFCC template did not significantly change the peak intensity when increasing the content of Cu impregnation into the sFCC framework, even if it contained Cu₂O and CuO, in accordance with the metal loading amount being relatively low.^{26,28}

XRF analysis was performed to confirm the elemental character and elemental composition presented in Table S1, which has a mass molar ratio of Si/Al between 1.1 and 1.0 by spent FCC catalyst and 3 wt % Cu-modified-spent FCC. In addition, the modification of spent FCC with Cu impregnation illustrated that the content of copper metal corresponds to the weight percentage of Cu-modified-spent FCC of approximately 0.461 wt %.

Figure 3 illustrates the adsorption and desorption isotherms of fresh FCC, spent FCC, and Cu-doped FCC, which

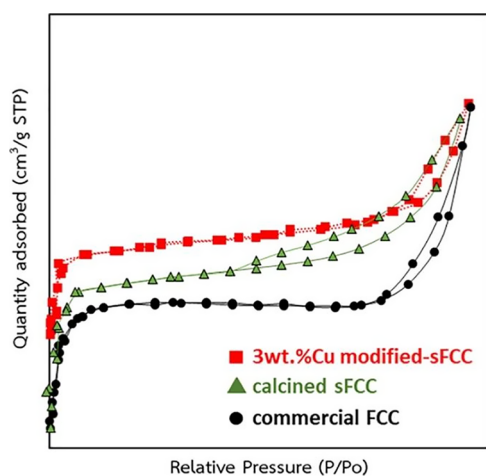


Figure 3. Adsorption–desorption isotherm.

determined the textural properties (pore volume, pore size, and specific surface area). The physicochemical properties of the FCC, sFCC, and Cu-modified sFCC catalysts are listed in Table 2. The small crystallites of CuO might be derived from the rate of nucleation being larger than the rate of nuclear increase with the content of Cu-modification to the sFCC parent template corresponding to the increasing Cu loading resulting in the crystallite size slightly increasing and the surface areas decreasing gradually.²⁸

Table 2. Characterization of the Catalyst Texture

catalyst	total surface area (m ² /g)	total pore volume (cm ³ /g)	average pore size (nm)
new FCC	413.7	1.12	2.06
sFCC	117.9	0.12	4.36
Cu-modified sFCC	116.3	0.13	4.55

3.2. Effect of Operating Conditions on Product Yield and Distribution.

3.2.1. Influence of Reaction Temperature on the Product Yield Distribution.

Generally, the temperature is the most influential operating parameter affecting the product yield and its distribution in pyrolysis or catalytic pyrolysis. In this study, the temperature is also the main influence on SLO/LDPE catalytic pyrolysis, which affects both SLO/LDPE by thermal decomposition and further cracking reactions via acid strength and active sites when the catalyst is used in the reaction. Figure 4 illustrates the effect of operating temperature on the product yield and distribution, whereas the constant conditions of the mass ratio 0.5:0.5 SLO/LDPE, time of reaction 45 min, the 0.3 wt % Cu-sFCC by 5 wt % mass molar of catalyst to the feedstock.

The product distribution according to the boiling point range illustrated that the distribution obtained at 400 °C mainly consisted of a long residue fraction due to the insufficient thermal decomposition of large hydrocarbon compounds of both SLO and LDPE into smaller hydrocarbon compounds that contained a large structure and were not suitable for catalytic pyrolysis through the porosity, acid strength, and active sites of the Cu-sFCC catalyst.^{11,20} Therefore, the selectivity of smaller hydrocarbon compounds, e.g., naphtha-like, kerosene-like, and diesel-like fractions, was very low compared to those at other operating temperatures or almost not present.

The selectivity of diesel-like fraction increased dramatically with the increased reaction temperature from 400 to 450 °C and decreased when temperature increased more than 450 °C because the thermal degradation of both LDPE and SLO at higher temperatures played an extreme role in accelerating the thermal degradation of LDPE,^{5,6,14,29–31} which resulted in the production of hydrogen radical and hydrocarbon radicals. Then, the rearrangement of both H-radical and hydrocarbon occurred to generate small amounts of hydrogen gas and hydrocarbon gas products,^{28,31} resulting in an enhanced hydrogen atmosphere in the catalytic reaction, which promoted the hydrogenation reaction coupled with H-transfer and β -scission of long-chain hydrocarbon compound into light alkane during the catalyst pyrolysis reaction.

The liquid product yield obtained from the catalytic copyrolysis of SLO/LDPE tended to decrease from 70.66 wt % (400 °C) to 68.94 wt % (425 °C) and 63.12 wt % (450 °C) and then markedly dropped to 55.76 wt % at 475 °C, causing continuous thermal cracking of middle hydrocarbon molecules into simpler small hydrocarbon gaseous products and leading to a secondary cracking reaction into noncondensable gaseous products.¹⁵ Furthermore, increasing the process temperature can enhance the catalytic pyrolysis of SLO/LDPE and decompose large hydrocarbon molecules into smaller hydrocarbons. Then, the catalytic reaction enhances the scission of middle compounds, promotes the hydrogen transfer reaction over the acidic active site of Cu-sFCC, and enhances the β -scission of middle compounds into a small linear alkane.^{26–28,31} As shown in Figure 4, the product distribution of the catalytic pyrolysis of SLO/LDPE over Cu-sFCC obtained at 400 °C consisted mainly of a long residue fraction of 42.91 wt %, while the proportions of diesel-like, kerosene-like, and naphtha-like residues were 13.74, 8.38, and 5.63 wt %, respectively. It seems that a low operating temperature was not enough to accelerate the thermal decomposition of large hydrocarbon molecules, especially from SLO, and could not enhance the catalytic activity of the copyrolysis of SLO/LDPE

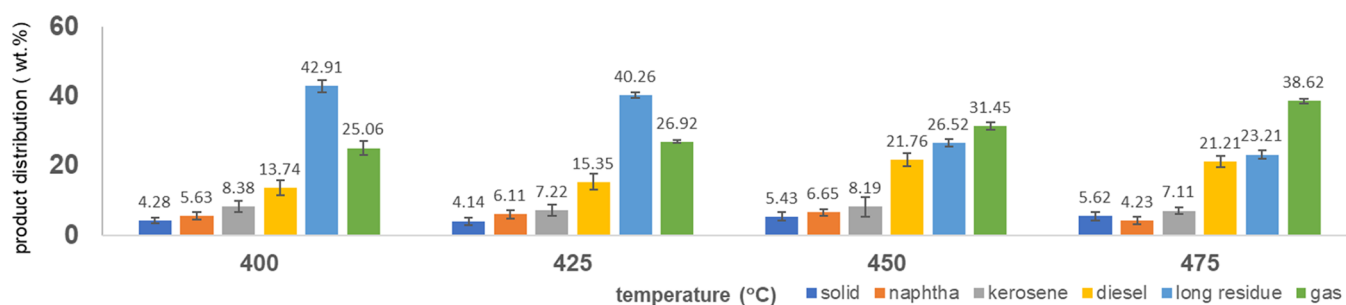


Figure 4. Effect of operating temperature on the product distribution of catalytic pyrolyzed oil from 0.5:0.5 mass molar of SLO/LDPE kept a constant reaction time of 60 min using 3 wt % Cu-modified-spent FCC at 10 wt % mass molar of the catalyst to the feedstock.

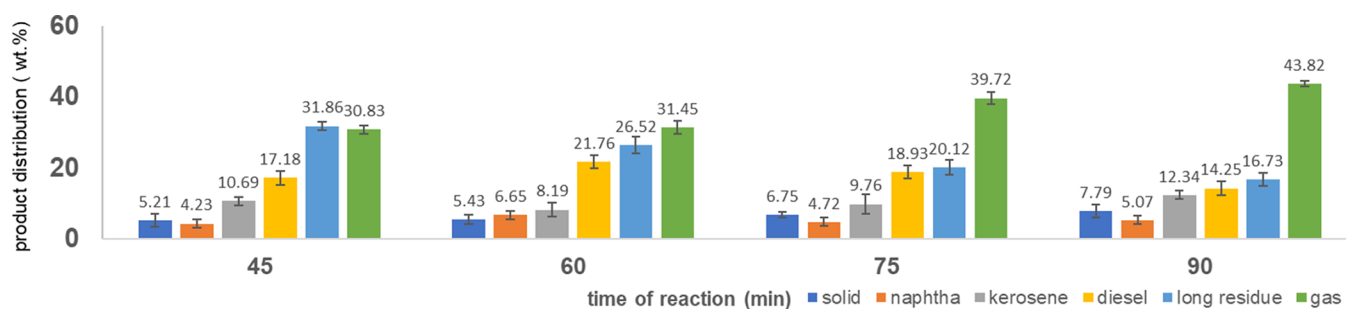


Figure 5. Effecting reaction time on product distribution of catalytic pyrolyzed oil from 0.5:0.5 mass molar of SLO/LDPE kept constant reaction temperature of 450 °C using 3 wt % Cu-modified-spent FCC at 10 wt % mass molar of catalyst to the feedstock.

because large hydrocarbon compounds could not arrange into middle hydrocarbon compounds by thermal degradation. Inappropriate large hydrocarbon compounds could not pass through the microporous structure of sFCC and inhibited the acidic active sites and pore structure of the Cu-sFCC catalyst.^{11,12} Additionally, the catalytic activity at acidic active sites of Cu-sFCC could not be completely illustrated mainly by the long residue fraction, and a relatively low amount of the diesel-like fraction was obtained according to the low pyrolysis temperature.

Increasing the operating temperature also illustrated the higher liquid yield and diesel-like fraction due to the high reaction temperature dramatically promoting the catalytic pyrolysis of SLO/LDPE, which can be explained by the fact that temperature could be predominantly attributed to the enhancement of the acceleration of the carbon–carbon degradation of long-chain hydrocarbon compounds. Hydrogen radicals and hydrocarbon radicals produced the hydrogen gaseous product and enhanced the carbon–carbon scission of the long residue fraction (C_{22+}) to smaller, hydrogenation, isomerization was also rearrangement of a middle hydrocarbon compound to the diesel-like fraction of C_{12} – C_{16} of linear alkane,^{26,28,32,33} which was achieved from the influence of both higher temperature and catalytic activity. However, it is notable that the gaseous yield was slightly increased from 25.06 wt % (400 °C) to 26.92 wt % (425 °C) and 31.45 wt % (450 °C). Therefore, increasing the reaction temperature from 425 to 450 °C enhanced the catalytic activity of the cracking reaction and promoted the degradation of large hydrocarbon compounds into smaller hydrocarbon compounds. Then, the catalytic pyrolysis of both pore-selective and acidic active sites was also affected by the appropriate rearrangement of middle hydrocarbon compounds by the cleavage of carbon–carbon bonds, hydrogen transfer, hydrogenation, and isomerization at the acidic active sites to obtain light alkanes and slightly

increased the amount of kerosene light and the small amount of naphtha-like fraction.

In contrast, the liquid product distribution obtained at 475 °C decreased to 55.76 wt %, kerosene-like (7.11 wt %) and diesel-like (21.21 wt %) were slightly changed, but the gaseous yield extremely increased to 38.62 wt %, all of those affected by the influence of thermal decomposition led to the decomposition of SLO and LDPE to hydrogen and hydrocarbon radicals, which obtained a high proportion of the small gaseous products, while the high temperature also enhanced the decomposition of a smaller compound and further the secondary cracking reaction of these light hydrocarbon compounds to the noncondensable gas rather than the effect of the catalytic pyrolysis reaction.^{26,28,34} This can be ascribed to the higher temperature of 450 °C also accelerating the cleavage of carbon–carbon bonds of the volatile toward small volatiles. Furthermore, the gaseous product yield increased obviously with increasing process temperature from 450 to 475 °C, while a slight increase in the amount of carbonaceous material was obtained at 475 °C of approximately 5.62 wt %. It seems that the high process temperature enhanced the decomposition of SLO and LDPE to noncondensable gas products, which may be influenced by the gradual increase in carbonaceous at the acidic active site, resulting in deactivated catalytic performance.^{32–34} Thus, thermal decomposition was only affected by the degradation of SLO and LDPE into smaller hydrocarbon gaseous products and further secondary cracking reactions into noncondensable gases,^{11,28,32} which notably increased to 38.62 wt % at a reaction temperature of 475 °C.

3.2.2. Influence of the Reaction Time on the Product Yield Distribution. Figure 5 shows the influence of reaction time on product yield and its distribution according to the boiling point range of catalytic pyrolysis of SLO and HDPE, which was carried out at a constant temperature of 450 °C using 1.0 wt %

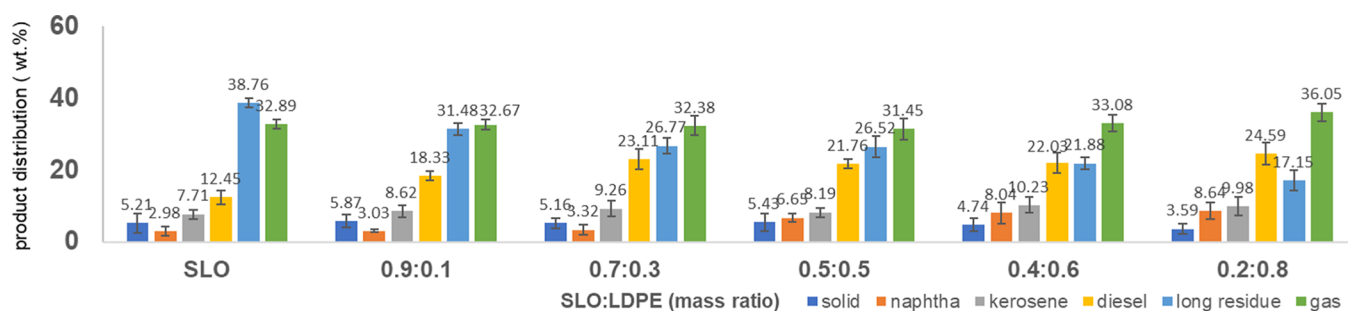


Figure 6. Effect of the SLO/LDPE mass ratio on the product distribution of catalytic pyrolyzed oil from the reaction temperature of 450 °C for 60 min using 3 wt % Cu-modified-spent FCC at 10 wt % mass molar of the catalyst to the feedstock.

Cu-sFCC catalyst with 5 wt % loading of the catalyst. When the reaction time was 45 min, the gaseous product yield was 30.83 wt %, the liquid yield was only 63.96 wt % and consisted of long residual, diesel-like, kerosene-like, and naphtha-like products of 31.86, 17.18, 10.69, and 4.23 wt %, respectively, while a small amount of solid residue was obtained.

Increasing the retention time results in the conversion of LDPE into a smaller hydrocarbon chain by the radical reaction to produce a more stable component, which enhances the promotion of hydrocarbon radicals and hydrogen gas to enhance the hydrogenation reaction of the middle alkane coupled with thermal degradation of SLOs into middle hydrocarbon molecules prior to the effect of temperature enhancing the promotion of cracking into small alkanes by the catalytic pyrolysis reaction. This enhances the acceleration of cracking at the metal active site over the sFCC into small alkane hydrocarbon compounds. Nevertheless, it seems that the short residence time insufficiently promotes the degradation of large hydrocarbon molecules of both SLO and LDPE to smaller compounds,^{5,8,28,35} resulting in the large hydrocarbon chain not passing through the pore structure of the sFCC and further cracking at the metal acidic active site of the catalyst. In contrast, at the short residence time, the pyrolyzed oil mainly consisted of long residue, and a slight increase in solid residue according to the thermal degradation of large hydrocarbon compounds is more effective than catalytic pyrolysis to obtain a middle hydrocarbon compound. Then, the depolymerization of hydrocarbon compounds occurred to obtain larger compounds.^{28,32}

At a pyrolysis time of reaction of 60 min, the thermal degradation of the medium hydrocarbon compounds was enhanced to smaller hydrocarbon compounds and then further affected by secondary cracking, leading to carbon–carbon bond cleavage of those compounds to shorten linear alkanes, which consisted of long residues, diesel-like, kerosene-like, and naphtha-like of 26.52, 21.76, 8.19, and 6.65 wt %, respectively, while the gaseous product yield slightly increased to 31.45 wt %, whereas the time of reaction increased, the desirable diesel-like fraction was quite increased while all of those small hydrocarbon compounds were continually cracking into smaller and secondary cracking to produce a large proportion of noncondensable gas (43.82 wt %) at the time of reaction increased to 90 min because the long residue fraction was also affected by the thermal degradation and catalytic pyrolysis under high temperature conditions. Both SLO and LDPE were decomposed into a middle hydrocarbon chain and continually cracked into a dramatically increased gas component as the reaction continued. In addition, when the time of reaction increased to 90 min, it was notable that the liquid yield tended

to decrease, while the gas yield dramatically increased owing to the appearance of carbonaceous compounds that inhibited acidity active sites at the catalyst surface and pore structure, resulting in catalytic deactivation. Thus, the catalytic performance tends to decrease when the reaction time increases, resulting in random carbon–carbon bond cleavage, which affects only the thermal decomposition of free radicals and enhances the scission of carbon–carbon bonds to obtain a large amount of small hydrocarbon compounds, enhancing the secondary cracking reaction and increasing the gas yield by continued thermal degradation over time.^{26,28,35}

3.2.3. Influence of the SLO/LDPE Mass Molar Ratio on the Product Yield Distribution. The effect of the ratio of LDPE blended to SLO (0.1:0.9 to 0.7:0.3) on the product yield distribution in the catalytic pyrolysis of SLO/LDPE was determined at a temperature of 450 °C, a reaction time of 60 min, 0.5 wt % Cu-modified sFCC and a catalyst mass molar to feedstock of 10 wt %, as illustrated in Figure 6. In particular, the hydrogen atmosphere is one of the limiting parameters in hydrocracking and hydrotreating. The influence of the initial hydrogen pressure has also been investigated in several studies. In this test, the catalytic copyrolysis of SLO/LDPE was not performed under the initial hydrogen gas atmosphere, but hydrogen gas was generated from the thermal decomposition of LDPE in the form of hydrogen radicals and hydrocarbon radicals to produce a small amount of hydrogen gas during catalytic copyrolysis. Herein, increasing the reaction temperature enhanced the production of hydrogen gas and small hydrocarbon gaseous products; therefore, the ratio of LDPE blended with SLO was also investigated.

The increase in the LDPE to SLO from 0.1:0.9 to 0.8:0.2 is compared with the catalytic pyrolysis of SLO alone, as represented in Figure 6. As seen in the comparative product distribution, the catalytic pyrolysis of SLO obtained a diesel-like selectivity of 12.45 wt % (diesel-like yield of 12.45 wt % and liquid yield of 61.90 wt %). The catalytic pyrolysis of SLOs alone is influenced by the reaction temperature, causing decomposition in the form of random hydrogen radicals and hydrocarbon radicals. Then, the interaction of these radicals enhances the scission of large hydrocarbon structures and cleavage of carbon–carbon bonds and carbon–hydrogen bonds to formulate smaller hydrocarbon compounds, but these are still large hydrocarbon compounds, resulting in difficulty reacting with the acid active sites and pore structure of the catalyst.^{5,19,22,30,31} Therefore, the catalytic pyrolysis of SLOs also obtained the product distribution, which is mainly in the large amount of long residue fraction and small noncondensable gaseous products.

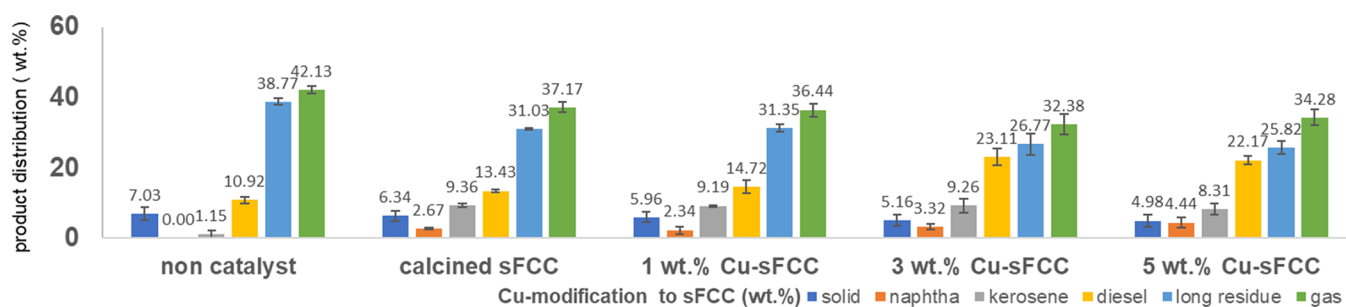


Figure 7. Effect of the amount of Cu loading to the sFCC on the product distribution of catalytic pyrolyzed oil from 0.7:0.3 mass molar of SLO/LDPE kept at a constant reaction temperature of 450 °C for 60 min using 10 wt % mass molar of catalyst to the feedstock.

When increasing the LDPE blended from 10% to SLO feedstock, the liquid yield and product distribution in the desired diesel-like fraction also increased from 12.45 to 18.33 wt %. It was pronounced that a low ratio of LDPE blended (0.1 LDPE to 0.9 SLO mass molar) still had a slightly significant effect on the catalytic copyrolysis of SLO/LDPE because the majority of the SLO component was also mostly converted to large hydrocarbon compounds with a lower amount of hydrogen atmosphere, which made it difficult to enhance the cleavage of carbon–carbon bonds in the SLO component. Thus, the product yield also contained mainly large hydrocarbon compounds that were too large to react with the acid active sites and could not diffuse through the microporous structure of the catalyst, causing the long residue fraction to be mainly obtained. It seems that SLO had a more prominent effect on the lower ratio of LDPE blended in catalytic copyrolysis and showed the product distribution and the low selectivity of the diesel-like fraction, which was similar to the catalytic pyrolysis of SLO alone.^{3,5,28,32,33}

By increasing the ratio of SLO/LDPE from 0.9:0.1 to 0.7:0.3, it was found that the product distribution of the diesel-like fraction was markedly increased from 18.33 to 23.11 wt % due to the thermal degradation of higher amounts of LDPE, which also increased the H-radicals and hydrocarbon radicals, enhancing the chain scission of LDPE and causing the production of medium hydrocarbon compounds. Herein, the H-donor from the thermal decomposition of LDPE enhances the carbon–carbon bond and carbon–hydrogen bond scission of SLOs from the initial thermal decomposition and enhances further catalytic reactions to produce smaller hydrocarbons.^{26,28,34} At the same time, the increase in LDPE blended with SLO exhibited a tendency to increase the diesel-like fraction to 24.59 wt %, according to the thermal decomposition of LDPE contributed to the H-radical and hydrogen radicals,^{26,31} which were attached to the H-donor and subsequently facilitated the interaction of both radicals with hydrogen gas production, which enhanced the hydrogenation, hydrotreatment and further catalytic reaction. Therefore, the selectivity of diesel-like molecules tends to increase. However, too much LDPE blended with SLO enhances the thermal decomposition of high-ratio LDPE due to the large proportion of small radicals acting as hydrogen. Therefore, hydrogen and hydrocarbon radicals may depolymerize and release hydrogen gas, including small hydrocarbon gases. Then, hydrocarbon transfer from the thermal degradation of LDPE and SLO acts as a hydrogen donor for SLO large hydrocarbon compounds, resulting in carbon–carbon scission to hydrogen gas, smaller hydrocarbon gas, and smaller hydrocarbon compounds. Then, further secondary reactions accelerate the catalytic cracking of

small hydrocarbon gaseous products to noncondensable gas, which also obviously increases.^{28,30,31,34}

3.2.4. Influence of Cu-Modification on the Spent FCC on the Product Yield Distribution. The effect of the copper concentration in the sFCC catalyst on the product yield distribution from 1 to 5 wt % in the catalytic pyrolysis of SLO/LDPE was determined under the following process conditions: 0.7:0.3 mass molar of SLO/LDPE, temperature of 450 °C, reaction time of 60 min, and catalyst mass molar to feedstock of 10 wt %, as illustrated in Figure 7.

The results of the wt % Cu-modification of the impregnate on the textural properties of the sFCC can be seen in Table 2. The increase in the wt % Cu impregnate also gradually decreases the pore volume and specific surface area. Notably, a high concentration of Cu was absorbed on the surface of the catalyst, while the micropore area was greater than the external surface area. It seems that the catalyst has many microporous channels. Thus, increasing the wt % Cu-modification in the sFCC template will decrease the large area on the external surface compared to that in the micropores, which shows that the increasing Cu-modification tends to be more absorbed in the external part than in the micropores.^{26,28}

The tests of the 3 wt % copper-impregnated sFCC show that with increasing copper concentration, the proportion of the long residue fraction greatly decreased to 26.77 wt %. Likewise, the diesel-like fraction tended to increase due to the effect of the thermal degradation reaction and catalytic activity, which also correlated with acidic active sites and high concentrations of copper. Notably, the increase in Cu impregnation contained too many acidic active sites,^{14,15,26} which accelerated the carbon–carbon bond decomposition during the high-temperature pyrolysis reaction. Then, the small volatile vapor can pass through the micropores of the sFCC. The results indicated that the role of the strong Brønsted acid catalyst was enhanced to improve the catalytic activity to cleave C–C bonds from the medium-length hydrocarbon chain to smaller compounds.

The 5 wt % impregnated sFCC catalyst containing the largest amount of total acid sites represents the highest noncondensable gas yield of approximately 34.28 wt %, and it was found that the relation between the sFCC parent catalyst and Cu-impregnated catalyst was likely due to sFCC having strong Brønsted acid sites,^{24,26,28,33} which are more favorable for the catalytic cracking reaction of long-chain hydrocarbons to smaller hydrocarbon chains and rearranged its structure at the pore structure, including the catalytic reaction, e.g., hydrogenation, hydrocracking, and isomerization. An increase in Cu impregnation mainly has too many acidic active sites, which are extremely enhanced due to the cleavage of carbon–carbon bonds and carbon–hydrogen bonds in large hydro-

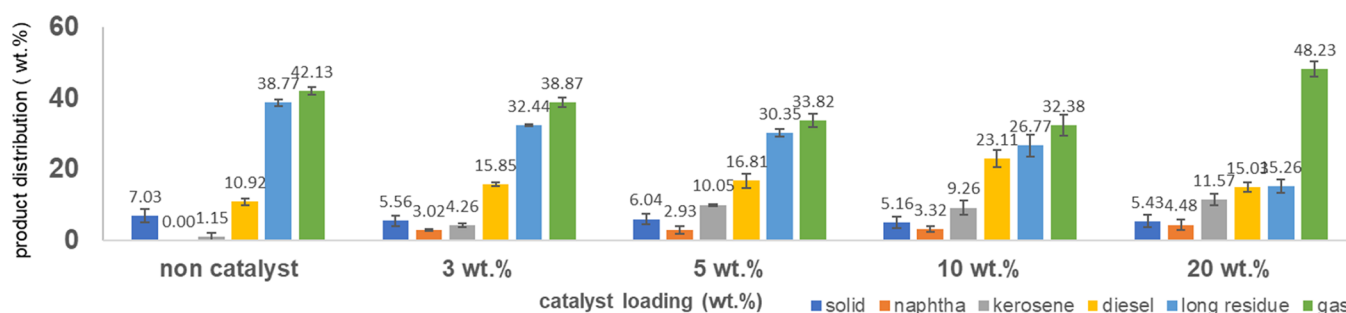


Figure 8. Effect of catalyst loading on the product distribution of catalytic pyrolyzed oil from 0.7:0.3 mass molar SLO/LDPE kept at a constant reaction temperature of 450 °C for 60 min using 3 wt % Cu-modified sFCC.

carbon compounds, likely the long residue fraction into simple linear alkanes. However, the high concentration of Cu impregnation may also inhibit the catalytic pyrolysis reaction under high-temperature conditions because the high relative acid active sites cracked the long residue fraction into smaller hydrocarbon compounds and further attributed the secondary cracking reaction to a slight increase in the gaseous product yield. Moreover, excessive Cu-impregnated sFCC showed a lower content of both kerosene-like and diesel-like fractions because copper inhibited the catalytic activity in the microporous structure, resulting in the middle volatile hydrocarbon compounds from thermal degradation not successively passing through the textural structure of the parent catalyst and having difficulty reacting with the acidic active site.^{9–11,26–28,33} Therefore, the product yield distribution of desirable products in both kerosene- and diesel-like fractions tended to decrease. It is obvious that the selectivity of diesel-like on all series of Cu-modified sFCC represented higher selectivity than that from the parent sFCC. In particular, the use of 3 wt % Cu-sFCC also obtained the highest liquid yield and diesel-like yield (62.46 wt %), resulting in the maximum selectivity of the desired diesel-like product (23.11 wt %). However, an excessive amount of Cu-modified sFCC could result in acidity and simultaneous coverage of the active sites on the sFCC and blockage of pores with a decrease in surface area, reducing the catalytic conversion of SLO/LDPE to the desired diesel-like product. Meanwhile, the yields of gas and carbonaceous coke were higher than those of the sFCC catalyst alone.

The results illustrated that 3 wt % is the optimum Cu-modified pm sFCC template causing the modified Cu-sFCC to increase the acid properties, acid active site and acid strength, affecting the catalytic cracking, further catalytic reaction, e.g., hydrogenation, hydrotreating, isomerization, and secondary reaction,^{15,16,28} resulting in the liquid product yield and the selectivity of the diesel-like fraction.

3.2.5. Influence of Catalyst Loading on the Product Yield Distribution. The mass ratio of the catalyst to feedstock is one necessary factor affecting the desirable pyrolysis product distribution. In this test, the catalytic pyrolysis of 0.7:0.3 by mass molar of SLO/LDPE, an operating temperature of 450 °C, and a reaction time of 60 min using 3 wt % Cu-modified sFCC were performed by several mass ratios of catalyst to feedstock from 3 to 20 wt % compared with no catalyst are listed in Figure 8.

As seen in Figure 8, the noncatalytic pyrolysis produced mainly a long residue fraction of 40.77 wt % in the liquid yield, 47.13 wt % in the gaseous yield, and the appearance of solid carbonaceous also obtained at 7.03 wt %. The result can be explained that noncatalytic pyrolysis cannot effectively convert

large hydrocarbon compounds of both SLO and LDPE into smaller molecules, but the effect of temperature only enhances the random thermal degradation of large hydrocarbon to smaller hydrocarbon, which resulted in the occurrence of a small amount of hydrogen and a middle hydrocarbon radicals. Both a middle hydrocarbon radical and hydrogen radical were also depolymerized and polymerized to form large hydrocarbon compounds that cannot undergo the hydrogen transfer reaction, hydrogenation, or isomerization,^{14,15,28} which usually occurs in the catalytic pyrolysis reaction. Therefore, only the thermal cracking of SLO/LDPE feedstock to smaller hydrocarbon compounds further influenced by high temperature enhanced the secondary cracking reaction and continually cracked the product into a noncondensable gaseous product.

In the catalytic pyrolysis of catalyst mass molar to SLO/LDPE feedstock from 3 to 20 wt %, the liquid product yield also slightly increased from 55.57 to 62.46 wt % when the catalyst loading was increased from 3 to 10 wt %, and then extremely dropped to 46.34 wt %, which also indicated that the catalytic cleavage of carbon–carbon bonds accelerated the large hydrocarbon compounds decomposed into middle hydrocarbon compounds.^{8,9,11,12,28} Nevertheless, when increasing the catalyst loading from 10 to 20 wt %, it was observed that the liquid product distribution tended not to significantly increase, but on the other hand, the gaseous product was also extremely increased to 48.23 wt %. Therefore, too much catalyst loading may not be beneficial for the conversion of SLO/LDPE into liquid yield and its desirable product distribution. Furthermore, it may not be commercial to use a high percentage loading of the invaluable metal catalyst in the pyrolytic reaction.^{2,10,31,35}

The product distribution of liquid products by several catalyst loadings illustrated that the conversion of the long residue fraction into smaller hydrocarbon compounds showed that the diesel-likeness increased from 15.85 to 23.11 wt % as the catalyst loading increased from 3 to 10 wt %. The increased proportion of diesel-like compounds can be attributed to increased metal active sites that enhance the cleavage of carbon–carbon bonds, which also accelerates the β -scission and H-transfer reaction of long-chain hydrocarbon compounds into middle hydrocarbon compounds.^{26,28} At this time, the secondary cracking reaction, hydrogenation, and isomerization may occur, resulting in enhanced improvement of moderate hydrocarbon compounds into light alkanes.²⁸ Therefore, the increased catalyst loading can be attributed to the increased catalytic performance, which promotes the catalytic activity of pyrolysis LDPE due to the catalytic active sites and pore-selective enhancement improving the scission of carbon–

Table 3. GC/MS Analyses of the Pyrolysis Oil from SLO/LDPE

peak no.	% area peak				chemical compounds	molecular formula
	noncatalytic pyrolysis SLO	catalytic pyrolysis SLO	catalytic pyrolysis LDPE	catalytic copyrolysis SLO/LDPE		
1			0.13		<i>n</i> -heptane	C ₇ H ₁₆
2				0.1	heptane	C ₇ H ₁₆
3		0.11			2,4-dimethyl-hexane	C ₈ H ₁₈
4			0.17	0.19	octane	C ₈ H ₁₈
5			1.39	2.51	nonane	C ₉ H ₂₀
6		0.09			2,3,4-trimethyl-hexane	C ₉ H ₂₀
7		0.13			2,4-dimethyl-heptane	C ₉ H ₂₀
8			2.52		<i>n</i> -decane	C ₁₀ H ₂₂
9				0.93	decane	C ₁₀ H ₂₂
10			2.03		undecane	C ₁₁ H ₂₄
11				3.81	undecane	C ₁₁ H ₂₄
12		0.98			1-dodecene	C ₁₂ H ₂₄
13		0.22	4.09		dodecane	C ₁₂ H ₂₆
14				3.45	dodecane	C ₁₂ H ₂₆
15					1-tridecane	C ₁₃ H ₂₈
16		1.03			tridecane	C ₁₃ H ₂₆
17	0.34		3.65	4.24	tridecane	C ₁₃ H ₂₈
18		0.48			1,3-tetradecadiene	C ₁₄ H ₂₆
19		0.25			tetradecane	C ₁₄ H ₃₀
20	0.11		3.27	2.29	tetradecane	C ₁₄ H ₃₀
21					1-pentadecene	C ₁₅ H ₃₀
22	1.15		4.14		pentadecane	C ₁₅ H ₃₂
23		0.24		3.55	pentadecane	C ₁₅ H ₃₂
24		1.63	2.01	2.19	hexadecane	C ₁₆ H ₃₄
25	0.11				1-heptadecene	C ₁₇ H ₃₄
26	0.13				3-heptadecene	C ₁₇ H ₃₄
27		1.21	0.49	0.39	heptadecane	C ₁₇ H ₃₆
28		1.36	0.71	0.23	octadecane	C ₁₈ H ₃₈
29	1.32				1-nonadecene	C ₁₉ H ₃₈
30		2.41	0.34	0.13	nonadecane	C ₁₉ H ₄₀
31		2.52		0.08	eicosane	C ₂₀ H ₄₂
32		2.99		0.29	heneicosane	C ₂₁ H ₄₄
33	1.36	0.92			2,4-dimethyl-eicosane	C ₂₂ H ₄₆
34	4.32	2.63		0.34	docosane	C ₂₂ H ₄₆
35	5.44	2.87			tricosane	C ₂₃ H ₄₈
36	1.68				1-tetracosene	C ₂₄ H ₅₀
37		1.11			tetracosane	C ₂₄ H ₄₈
38	4.81				1-hexacosene	C ₁₈ H ₃₈
39	2.02	1.68			2-methyl-hexacosane	C ₂₆ H ₅₂
40	1.31				3-methyl-heptadecane	C ₂₇ H ₅₆
41	0.92				2-methyl-octadecane	C ₁₉ H ₄₀

carbon bonds, hydrogenation, and isomerization to the diesel-like fraction.

Increasing the catalyst loading to 20 wt % in the catalytic pyrolysis of SLO/LDPE resulted in a high conversion of the long residue fraction to smaller hydrocarbon compounds and a high proportion of gaseous products to 48.23 wt %, but notably, a diesel-like fraction dropped to 15.26 wt %. The middle hydrocarbon compounds may not be converted to light alkanes due to the higher catalytic site that continuously facilitates the cleavage of carbon–carbon bonds of light alkanes to a smaller hydrocarbon gas. This indicated that the catalyst had the ability to break the carbon–carbon and carbon–hydrogen bonds present in the hydrocarbons, which resulted in increased carbon–carbon bond-breaking reactions at higher temperatures or with increased catalytic sites. When the catalyst loading was increased to 20%, more atomic bonds

were broken and their production increased as the percentage of catalyst was increased. As the catalyst increased, the number of carbon–carbon bonds broken increased,^{26,28} which accelerated the conversion of light compounds into a large proportion of noncondensable gas products.

The presence of the catalyst can accelerate the production of hydrocarbon, and its further hydrogenation in the catalytic pyrolysis of SLO/LDPE enhances the promotion of cracking the long-chain hydrocarbon to light alkane by the cleavage of carbon–carbon bonds and carbon–hydrogen bonds, then hydrogen transfers, hydrogenation at the acidic active site with the consumption of hydrogen radical and hydrogenation also occurred,^{28,32–35} resulting to the proportion of diesel-like in the liquid product increased that can see mainly light alkane having a carbon range number of C₁₂–C₁₈.

Table 4. Ultimate Analyses and Physicochemical Analysis of the Optimized Pyrolysis Oil^a

	raw SLO	noncatalytic pyrolysis SLO	catalytic pyrolysis SLO	catalytic copyrolysis SLO/LDPE	standard test method
ultimate analysis (wt %)					
C	79.55	85.79	87.56	86.61	
H	12.59	10.65	11.48	13.39	
O	7.72	3.56	0.96	n.d.	
N	0.14	n.d.	n.d.	n.d.	
S	n.d.	n.d.	n.d.	n.d.	
H/C (mass molar/mass molar)	1.90	1.49	1.57	1.86	
O/C (mass molar/mass molar)	0.07	0.03	0.01	0.00	
higher heating value (MJ/kg)	43.49	43.57	45.82	48.40	calculation
higher heating value (MJ/kg)	41.65	43.02	45.29	48.03	ASTM D240
kinematic viscosity (mm ² /s)	44.07	7.71	6.95	2.05	ASTM D445-19
modification acid number (mg _{KOH} /g)	5.31	0.52	0.36	0	ASTM D664-07

^an.d. = not detected.

3.3. Compositional Study and Fuel Properties.

3.3.1. GC/MS Analyses. The pyrolysis oil obtained from the catalytic copyrolysis of SLO/LDPE using Cu impregnated into a spent FCC catalyst in a microbatch reactor was investigated by using gas chromatograph mass spectrometry and consisted of more than 100 different compounds, which made it difficult to take into consideration all compounds detected through GC/MS analysis. In this research, GC/MS is useful for identifying the species of pyrolysis oil at several retention times. The percentages of the peak area, chemical formulas, and molecular weights are listed in Table 3, but the area provided by the GC/MS is not proportional to the amount of that compound in the liquid oil that consisted of many carbon numbers of hydrocarbon compounds. Nevertheless, the GC/MS technique presented only chemicals with main peaks, which are illustrated of those in the % peak area. In addition, the chemical compounds were also divided into functional groups representing the occurrence of aliphatic hydrocarbons of carbon ranging from C₇ to C₁₈ compared with the pyrolysis of SLO alone. To determine the main commons present in copyrolysis oil at a 0.7:0.3 mass molar ratio of SLO/LDPE under the optimal process conditions of 450 °C and a reaction time of 60 min, 3 wt % Cu was impregnated into the sFCC catalyst at 10 wt % mass molar catalyst loading to feedstock and compared with the catalytic pyrolysis of individual SLO and LDPE and noncatalytic pyrolysis of SLO alone under the same operating conditions. The main compounds and their corresponding relative area % with molecular formulas are represented in Table 3.

The GC/MS chromatograph obtained from the catalytic copyrolysis oil matched with that from the NIST library, representing a mostly linear alkane in carbon number ranging from C₇ to C₁₈, which is subdivided into C₇–C₁₁ (naphtha and kerosene-like fraction), C₁₂–C₁₈ (diesel-like fraction), and C₁₉⁺ (long residue fraction) according to the simulation distillation gas chromatograph, consisting of nonane, undecane, dodecane, tridecane, tetradecane, pentadecane, and hexadecane with peak areas of 2.51, 3.81, 3.45, 4.24, 2.29, 3.55, and 2.19, respectively, which were found to be the major chemical compounds in the desirable diesel-like products. Meanwhile, the catalytic pyrolysis of SLO showed that tridecane, hexadecane, heptadecane, octadecane, nonadecane, eicosane, heneicosane, docosane, tricosane, tetracosane, and 2-methyl-hexacosane with relative peak areas of 1.03, 1.63, 1.21, 1.36, 2.41, 2.52, 2.99, 2.63, 2.87, 1.11, and 1.68, respectively.

The results reveal that catalytic pyrolysis of SLO alone had a higher area of C₂₀⁺ hydrocarbon compounds and consisted of a very small amount of C₇–C₁₉. Furthermore, thermal cracking of SLO was mainly observed for pentadecane, 1-nonadecene, 2,4-dimethyl-eicosane, docosane, tricosane, 1-tetracosene, 1-hexacosene, 2-methyl-hexacosane and 3-methyl-heptadecane with relative peak areas of 1.15, 1.32, 1.36, 4.32, 5.44, 1.68, 4.81, 2.02, and 1.31, respectively. Most of these compounds represented long-chain hydrocarbon compounds that could not be converted into the desirable diesel-like products due to the limit of random carbon–carbon bonds cleavage, depolymerization and further repolymerization to formulated larger hydrocarbon compounds that cracked to smaller hydrocarbon compounds.^{3,14,15,28,31,36} In contrast, the blending of LDPE in the catalytic copyrolysis shifted to the distribution of a diesel-like fraction, and an increasing trend of C₁₂–C₁₈ linear alkanes was observed with a higher proportion than that of pyrolysis oil obtained from the reaction of SLO alone.

Furthermore, notably, C₂₂⁺ hydrocarbon compounds were present from the noncatalytic pyrolysis of SLO, while the decline in long-chain hydrocarbon compounds included the disappearance of C₁₉⁺ compounds from the catalytic pyrolysis of SLO/LDPE according to the GC/MS results, as presented in Table S7. It seems that the introduction of catalysts increased the total percentage of the relative peak area of C₈–C₁₈ hydrocarbon from 6.65% area peak to 23.78% area peak. A substantial increase in the relative peak area was present in catalytic copyrolysis, revealing that the thermal degradation of LDPE established by a small hydrogen gas and further catalytic cracking reaction plays a key role in the production of a hydrogen atmosphere and acid active sites, resulting in enhanced promotion of hydrogenation, hydrotreating, and hydrocracking of long-chain hydrocarbons of both SLO and LDPE, favoring the cracking of middle hydrogen compounds into smaller hydrocarbon molecules. Further catalytic reactions of smaller compounds may engage in isomerization and oligomerization reactions and convert them to linear alkanes with carbon numbers ranging from C₁₂ to C₁₈. Although this study pyrolysis process does not take place with the influence of an initial hydrogen pressure enhanced to promote the hydrogenation to the unsaturated hydrocarbon compounds during the catalytic pyrolysis and further cracking reaction, the catalytic copyrolysis reaction of SLO and LDPE to the alkane hydrocarbon compounds which contain carbon 7–18 atom. This chemical reaction can be described as LDPE being

Table 5. Analyses of Gaseous Components Using Gas Chromatograph^a

experiment	gas composition (wt %)							
	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	iso C ₄ H ₁₀	C ₄ H ₁₀	C ₄ H ₈
SLO noncatalyst	n.d.	1.84	4.22	3.68	7.99	16.65	7.22	3.18
SLO/LDPE noncatalyst	1.87	4.11	3.77	0.60	12.28	12.47	8.03	0.00
SLO/LDPE 1 wt %Cu-sFCC	3.31	7.13	7.47	n.d.	9.55	8.97	n.d.	n.d.
SLO/LDPE 3 wt %Cu-sFCC	3.21	7.16	7.76	n.d.	6.88	7.37	n.d.	n.d.
SLO/LDPE 5 wt %Cu-sFCC	3.12	9.21	7.51	n.d.	7.36	7.08	n.d.	n.d.

^an.d. = not detected.

thermally degraded into a radical, and further cracking via hydrogen transfer enhances the cracking reaction of the long-chain hydrocarbon polymer into smaller hydrocarbon compounds coupled with the formation of hydrogen gas to promote hydrogenation to unsaturated hydrocarbon compounds.^{13,20,32,36} The results confirmed that both LDPE and the catalyst cracked volatile vapor during the thermal decomposition of SLO under a small amount of hydrogen atmosphere, and the acid strength from metal modified to spent FCC at the active site of the catalyst favored the production of linear alkanes with carbon ranging from C₁₂ to C₁₈. This might be due to the large hydrocarbon compounds from both SLO and LDPE that consisted of C₂₂⁺ hydrocarbon chains being degraded from the influence of high temperature to form radicals.^{26,28} Then, the cleavage of carbon–carbon bonds and beta-scission enhanced by acid active sites cracked and converted into a linear C₇–C₁₆ alkane.

3.3.2. Physicochemical Analyses of Optimized Pyrolysis Oil. Physicochemical analyses of pyrolysis oil were performed to investigate the characteristics of liquid fuels according to the standard specifications endorsed by the ASTM standard and were applied to pyrolysis oil obtained from this work. Ultimate and physicochemical analyses of pyrolysis oil obtained from the optimal process conditions of 0.7:0.3 mass molar ratio of SLO/LDPE using 3.0 wt % Cu impregnated into the spent FCC catalyst at 10 wt % catalyst loading to feedstocks compared with noncatalytic pyrolysis of SLO and catalytic pyrolysis of individual SLO are given in Table 4.

The H/C ratio of the optimized catalytic copyrolysis oil indicated the saturation level of carbon–carbon bonds,^{6,33,37,38} which decreased the H/C ratio, indicating a designated formation of compounds containing carbon–carbon bonds as a result of thermal degradation of LDPE to small hydrogen gaseous production, and then catalytic cracking under the initial hydrogen atmosphere at high temperature enhanced the production of a linear C₇–C₁₈ alkane.

The HHV of noncatalytic pyrolysis of SLO, catalytic pyrolysis of individual SLO, and catalytic copyrolysis of SLO/LDPE was performed in an adiabatic bomb calorimeter according to ASTM D240 and was 43.57, 45.29, and 48.03 MJ/kg, respectively. Moreover, the HHV was also calculated according to Dulong's equation³⁹

$$\text{HHV (MJ/kg)} = 0.338C + 1.428 \left[H - \left(\frac{O}{8} \right) \right] + 0.095S \quad (4)$$

where C, H, O, and S are carbon, hydrogen, oxygen, and sulfur in mass percentage, respectively, which were also obtained from the elemental analysis. The calculation results illustrated in Table 4 were quite similar to the HHV analyses from the bomb calorimeter. Notably, the decreasing H/C ratio in the process of catalytic copyrolysis was observed to increase the

HHV (48.40 MJ/kg) compared to that of noncatalytic pyrolysis oil and catalytic pyrolysis of SLO alone (45.82 MJ/kg).

The acidity of the pyrolysis oil was represented in terms of the modified acid number (MAN), which was not very different, and the noncatalytic pyrolysis of SLO, catalytic pyrolysis of SLO and catalytic pyrolysis of SLO/LDPE contained MANs of 0.52, 0.36, and 0.00 mg KOH/g, respectively. Notably, the constituents of the used lubricants mainly consisted of carbon and hydrogen, with only a very small amount of oxygen and nitrogen. Therefore, the pyrolysis process also obtains pyrolysis oils that are components of hydrocarbon chains of different lengths.^{40–42}

The catalytic copyrolysis oil showed a lower kinematic viscosity value (2.05 mm²/s) than the noncatalytic pyrolyzed oil (7.71 mm²/s) and catalytic pyrolysis oil from an individual SLO (6.95 mm²/s), while the kinematic viscosity of the spent SLO collected from the garage was also 44.07 mm²/s. These results indicate that SLO is mainly composed of larger hydrocarbon chains, and the operational temperature in the reactor may affect the limit of random degradation, resulting in the depolymerization and formation of large hydrocarbon chains. Meanwhile, the pyrolysis process of SLO was also influenced by high-temperature conditions, causing the degradation of the hydrocarbon chain to a random free radical to form hydrocarbon radicals and depolymerization^{6,28,31} and may be further repolymerized to formulate large hydrocarbon molecules as well. Therefore, the catalytic pyrolysis of SLO alone and catalytic copyrolysis of SLO/LDPE were influenced by thermal decomposition to shorten hydrocarbon chains, which is sufficient for the further secondary reaction of large hydrocarbon chains that can continually undergo catalytic activity, e.g., hydrogenation, hydrocracking, hydrotreating, and further secondary cracking. This resulted in the scission of carbon–carbon bonds, decreasing the chain length to shorten hydrocarbon compounds. Then, the hydrogenation reaction and further cracking reaction enhance the improvement of a saturated small hydrocarbon chain into a desirable diesel-like fraction consisting of a shortened alkane in carbon number ranging from C₇ to C₁₈.

The physicochemical analyses showed that the properties of pyrolysis oil were also quite similar and met the standard requirements of diesel grade.^{19,20,29} Therefore, it is a beneficial alternative way to convert waste lubricant oil from the garage via catalytic pyrolysis into diesel-like oil, while the catalytic pyrolysis of SLO with blended waste LDPE could be a successive process of both quantitative and qualitative production of alternative fuels^{4,14,29,30} and enhance attraction to the circular economy in several countries.

3.4. Gas Chromatograph Analyses of Gaseous Products. Table 5 presents the compositions of the gaseous product from the catalytic copyrolysis of SLO and LDPE at the

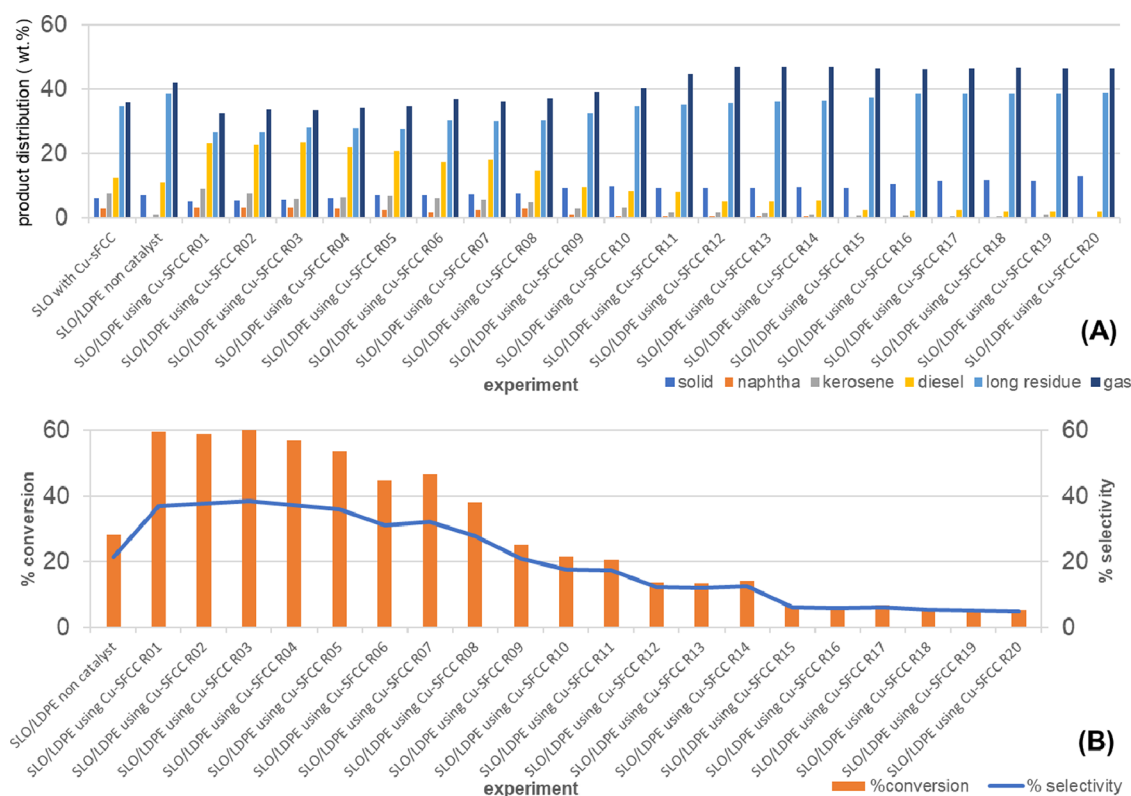


Figure 9. Reusability study of the 3 wt % Cu-modified sFCC catalyst. (A) Product distribution of catalytic copyrolysis from 0.7:0.3 mass molar SLO/LDPE kept at a constant reaction temperature of 450 °C for 60 min using 3 wt % Cu-modified sFCC catalyst at 10 wt % catalyst loading compared with catalytic pyrolysis of SLO alone and noncatalytic copyrolysis of SLO/LDPE (B) % conversion and % selectivity of diesel-like fraction from the cycle of reusable 3 wt % Cu-modified sFCC catalyst.

optimum process condition (temperature of 450 °C, reaction time of 60 min, using the 1–5 wt % Cu-modification on spent FCC catalyst at 10% catalyst loading). The gaseous products obtained from the pyrolysis of individual SLOs without catalyst, the catalytic pyrolysis of SLO and the catalytic copyrolysis of SLO/LDPE were also analyzed using a gas chromatograph were composed of hydrogen, methane, ethane, ethene, propane, iso-butane, butane, and butene.

As seen from Table 5, notably, the noncatalytic pyrolysis of individual SLOs mainly contained C₃ to C₄ hydrocarbon gases, and the composition of the gaseous products consisted of CH₄, C₂H₆, C₂H₄, C₃H₈, C₄H₁₀ and C₄H₈, while the formation of H₂ did not occur due to thermal degradation enhancing the random decomposition of long-chain hydrocarbons to middle hydrocarbon compounds. Then, cracking reactions and further secondary reactions of the medium volatile vapor occurred to produce a large amount of gas.

CH₄ is produced by the breakdown of hydrocarbon chains at the end of the chain, resulting in free hydrocarbon radicals, e.g., CH₂ radicals and CH₃ radicals, that will bond with hydrogen radicals from the thermal degradation of LDPE. Meanwhile, the thermal degradation of LDPE promoted the random decomposition of long-chain hydrocarbon compounds and enhanced the production of hydrogen radicals and hydrocarbon radicals. This noncatalytic copyrolysis of SLO/LDPE will produce hydrogen gas.

In particular, the effect of using the modified Cu on the sFCC parent template mainly has too many acidic active sites, which in addition to promoting the cleavage of carbon–carbon bonds and carbon–hydrogen bonds in large hydrocarbon compounds both of LPDE and SLO, resulted in increased

carbon–carbon bond breaking reactions at higher temperatures or with increased catalytic sites that cause secondary reactions at high temperatures, hydrocarbon breakdown, and oxidation, likely the long residue fraction compounds to light hydrocarbon gas. Additionally, the influence of the copper metal modification on the spent FCC catalyst will aid in the production of hydrogen and the breakdown of C₃–C₄ gases to smaller amounts by the secondary decomposition of volatile matter to hydrogen gas and light hydrocarbon gas products. Notably, therefore, an increase in %Cu-modified sFCC also leads mainly to increased production of H₂, CH₄, and olefin changes, which were formed during thermal cracking and enhanced the breakdown of a middle volatile vapor due to the strong acid site and textural structure of the catalyst. The appearance of C₂H₄, C₂H₆, and C₃H₈ hydrocarbon gases might be attributed to the degradation of volatile vapor. Then, secondary reactions also converted lower molecular weight hydrocarbons to C₂–C₃ gases.

3.5. Catalyst Reusability. To study catalyst activity, catalyst reusability is a significant parameter to consider. The catalyst reusability study for each experiment was performed in a 70 cm³ microbatch reactor by assuming that the reaction was isothermal at the set temperature for each batch of reactants under the optimal conditions of SLO and LDPE (by 0.7/0.3 mass ratio), an initial pressure of nitrogen gas of 1 bar, a constant liquid volume at 450 °C, and a reaction time of 60 min with 3 wt % Cu-modified sFCC at 10 wt % catalyst loading. After the reaction finished, the spent catalyst was separated and collected after finishing the reaction, dried, weighed, and then directly used before the next reaction. The

products were collected and therefore analyzed and compared to the noncatalytic pyrolysis system.

The selectivity of the diesel-like fraction was determined from the relative reaction of the diesel-like fraction and liquid fraction on the catalytic copyrolysis reaction, while the conversion of the long residual to the diesel-like fraction could also be determined from the proportion of the long residue from the noncatalytic copyrolysis of SLO/LDPE to a diesel-like fraction in each catalytic copyrolysis experiment, as described in eqs 5 and 6, respectively:

$$\% \text{ selectivity} = \frac{\text{wt \% of diesel like fraction}}{\text{wt \% of liquid fraction}} \times 100 \quad (5)$$

$$\begin{aligned} \% \text{ conversion} \\ = \frac{(\text{wt \% of long residue}_{\text{non cat}} - \text{wt \% of diesel like})}{\text{wt \% of long residue}_{\text{non cat}}} \\ \times 100 \end{aligned} \quad (6)$$

Figure 9A illustrates the product distribution of catalytic copyrolysis compared with catalytic pyrolysis of SLO alone and noncatalytic copyrolysis of SLO/LDPE, while Figure 9B represents the reusable catalyst on the selectivity of diesel-like and the % conversion of long residue to diesel-like. The selectivity of diesel-like compounds and the % conversion of long residue to diesel-like fraction were relatively stable, reaching a maximum % selectivity of diesel-like compounds at 37.64 ± 0.65 and % conversion of long residue to diesel-like compounds of 59.01 ± 1.36 when applied the 3 wt % Cu-modified sFCC at 10 wt % catalyst loading in the catalytic copyrolysis reaction at the fourth cycle and decreasing with increasing reuse time of the catalyst. After that, the selectivity of diesel-like species gradually decreased when the reuse cycle of the catalyst increased to 6 times and then dramatically decreased until catalytic copyrolysis occurred 9 times. At the ninth cycle of the reusability study, the yield of the diesel-like fraction, the selectivity of the diesel-like species, and the conversion of long residue to diesel-like species decreased to 9.72 wt %, 21.02%, and 25.07%, respectively.

As shown in Figure 9B, the ninth cycle of reused catalyst decreased the % selectivity of diesel-like to 21.02%, while the conversion of long residue to diesel-like catalyst markedly decreased from 38.20% (at the eighth cycle) to only 21.02%. Additionally, when comparing the experimental results of reusing the catalyst in the ninth cycle with the copyrolysis of SLO/LDPE without the catalyst, it was found that both the % selectivity and the % conversion of long residue were lower than those of copyrolysis without the catalyst (%selectivity of 21.48 and %conversion of 28.17). In addition, it is also worth noting that the catalyst reusability showed that the % solid yield tended to increase from 5.16 to 7.72 wt % at the eighth cycle, which was due to the formation of carbonaceous on the surface structure of the catalyst and a significant increase to 9.45 wt % at the ninth cycle of reused catalyst, consistent with the trend of increasing % gas yield. The gas yield illustrated a slight increase in gas yield when using the reused catalyst from the first cycle (32.38 wt %) to the fifth cycle (34.89 wt %) and then continuously increased the % yield of noncondensable gas from 36.17 wt % (sixth cycle) to 46.50 wt % at the 20th cycle of reused catalyst. The catalyst reusability study indicated that the catalytic copyrolysis reached low activities after the eighth cycle without regeneration due to the 3 wt % Cu-modified sFCC deactivation by carbonance in accordance with both

surface acidity and inside of pore structure, which caused the blockage of pores and active sites, leading to catalyst deactivation affecting the decreased conversion of large hydrocarbon compounds to diesel-like fractions, while the gaseous component also increased due to the primary role of thermal degradation.

4. CONCLUSIONS

This study has shown that SLO and LDPE catalytic copyrolysis using a spent FCC catalyst has been successfully performed in a custom-built microreactor. The findings demonstrate the optimum process conditions to obtain the highest proportion of liquid fraction of 62.56 ± 2.77 wt % at a temperature of 450 °C and a reaction time of 60 min by using 3 wt % Cu-modified to the spent FCC parent template at 10 wt % mass molar catalyst loading to feedstock and show a remarkable effect of SLO with LDPE blended when used as feedstock in copyrolysis. On that, the yield of the diesel-like fraction increased by 23.11 ± 2.88 wt % compared to that of pyrolysis of SLO on an individual basis, which was only 12.45 ± 1.92 wt % under these same conditions. The higher pyrolysis temperature converted the complex hydrocarbon chain into aliphatic hydrocarbons and then into aliphatic and aromatization-derived middle aliphatic hydrocarbon molecules. Additionally, the addition of metal modification over the spent FCC catalyst illustrated that the acid active site of the catalyst resulted in a catalytic cracking and further secondary reaction leading to an increase of light hydrocarbon compounds. The diesel-like fuel range products can be obtained in LDPE-added copyrolysis under the desired process conditions that had a successive production on the diesel-like product distribution and promoted the production of aliphatic hydrocarbon compounds. The present results suggested copyrolysis of SLO with waste plastic as a suitable choice for waste disposal and the addition of metal modified on spent catalyst is a more favorable process for enhancement toward a good potential alternative of conventional fuel. The importance of applying a circular economy approach to the conversion of several wastes to alternative fuel production is also highlighted.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c05823>.

Additional information on XRF analyses of several catalysts; effect of operating conditions on the product distribution; total percentage relative to the peak area of C₇-C₁₈ fraction from GC/MS analyses; and reusability study of the 3 wt % Cu-modified sFCC catalyst (PDF)

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W.C.: conceptualization, methodology, investigation, visualization, validation, writing—original draft, review & editing, and funding acquisition. N.P.: investigation and visualization. A.P.: visualization and writing—original draft. T.V.: conceptualization, resources, validation, and writing—review & editing.

Notes

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REFERENCES

- (1) Patel, N.; Shadangi, K. P. Characterization of waste engine oil (WEO) pyrolytic oil and diesel blended oil: fuel properties and compositional analysis. *Mater. Today Proc.* **2020**, *33*, 4933–4936.
- (2) Hussain, Z.; Santhoshkumar, A.; Ramanathan, A. Assessment of pyrolysis waste engine oil as an alternative fuel source for diesel engine. *J. Therm. Anal. Calorim.* **2020**, *141*, 2277–2293.
- (3) Ucar, S.; Ahmet, R.; Özkan, S. K. Co-pyrolysis of waste polyolefins with waste motor oil. *J. Anal. Appl. Pyrolysis* **2016**, *119*, 233–241.
- (4) El-Mekkawi, S. A.; El-Ibiari, N. N.; Attia, N. K.; El-Diwani, G. I.; El-Arady, O. A.; Morsi, A. K. E. Reducing the environmental impact of used lubricating oil through the production of fuels by pyrolysis. *Environ. Nanotechnol. Monit. Manage.* **2020**, *14*, No. 100308.
- (5) Patel, N.; Shadangi, K. P. Thermochemical conversion of waste engine oil (WEO) to gasoline-rich crude oil. *J. Mater. Cycles Waste Manage.* **2020**, *22*, 536–546.
- (6) Santhoshkumar, A.; Ramanathan, A. Recycling of waste engine oil through pyrolysis process for the production of diesel like fuel and its uses in diesel engine. *Energy* **2020**, *197*, No. 117240.
- (7) Wan Mahari, W. A.; Zainuddin, N. F.; Chong, C. T.; Lee, C. L.; Lam, W. H.; Poh, S. C.; Lam, S. S. Conversion of waste shipping oil into diesel-like oil via microwave-assisted Pyrolysis. *J. Environ. Chem. Eng.* **2017**, *5*, 5836–5842.
- (8) Breyer, S.; Mekhitarian, L.; Rimez, B.; Haut, B. Production of an alternative fuel by the copyrolysis of landfill recovered plastic wastes and used lubrication oils. *Waste Manage.* **2017**, *60*, 363–374.
- (9) Ferella, F.; D'Adamo, T.; Leone, S.; Innocenzi, V.; Michelis, I. D.; Vegliò, F. Spent FCC E-Cat: Towards a Circular Approach in the Oil Refining Industry. *Sustainability* **2019**, *11* (1), 113.
- (10) Mahdi, S.; Nader, M. Catalytic pyrolysis of oil sludge using the nano alumina powder. *Energy* **2023**, *70*, No. 126954.
- (11) Alonso-Fariñas, B.; Rodríguez-Galán, M.; Arenas, C.; Torralvo, F. A.; Leiva, C. Sustainable management of spent fluid catalytic cracking catalyst from a circular economy approach. *J. Waste Manage.* **2020**, *110*, 10–19.
- (12) Jialin, G.; Bo, L.; Yonggang, W.; Shiwei, Z.; Hua, W. Cracking of waste engine oil in the presence of Fe₃O₄. *Energies* **2023**, *16* (2), 665.
- (13) Mustayen, A. G. M. B.; Rasul, M. G.; Wang, X.; Hazrat, M. A.; Negnevitsky, M.; Jahirul, M. I. Impact of waste-plastic-derived diesel on the performance and emission characteristics of a diesel engine under low load conditions. *Energy Convers. Manage.* **2023**, *2831*, No. 116936.
- (14) Padmanabhan, S.; Parthasarathy, M.; Vinod Kumar, T.; Muthuraman, V.; Muraliraja, R.; Ganesan, S. Environmental impact of waste plastic pyrolysis oil on insulated piston diesel engine with methoxyethyl acetate additive. *Pet. Sci. Technol.* **2023**, *41* (10), 1113–1130.
- (15) Mangesh, V. L.; Tamizhdurai, P.; Santhana Krishnan, P.; Narayanan, S.; Umasankar, S.; Padmanabhan, S.; Shanthi, K. Green energy: Hydroprocessing waste polypropylene to produce transport fuel. *J. Clean. Prod.* **2020**, *276*, No. 124200.
- (16) Mangesh, V. L.; Padmanabhan, S.; Tamizhdurai, P.; Ramesh, A. Experimental investigation to identify the type of waste plastic pyrolysis oil suitable for conversion to diesel engine fuel. *J. Clean. Prod.* **2022**, *246*, No. 119066.
- (17) Mangesh, V. L.; Perumal, T.; Subramanian, S.; Padmanabhan, S. Clean Energy from Plastic: Production of Hydroprocessed Waste Polypropylene Pyrolysis Oil Utilizing a Ni–Mo/Laponite Catalyst. *Energy Fuels* **2020**, *34* (7), 8824–8836.
- (18) Hwang, K.-R.; Choi, S.-A.; Choi, I.-H.; Lee, K.-H. Catalytic cracking of chlorinated heavy wax from pyrolysis of plastic wastes to low carbon-range fuels: Catalyst effect on properties of liquid products and dechlorination. *J. Anal. Appl. Pyrolysis* **2021**, *155*, No. 105090.
- (19) Dutta, N.; Gupta, A. An experimental study on conversion of high-density polyethylene and polypropylene to liquid fuel. *Clean Technol. Environ. Policy* **2021**, *23*, 2213–2220.
- (20) Raj, B. K.; Jyothi, Y.; Kanasani, P.; Siva Gangadhar, D. The best suitable alternative to diesel in a compression ignition engine between waste plastic oil and waste tire oil blends with diesel. *Energy Source, Part A* **2020**, *42* (22), 2731–2741.
- (21) Krishnaraj, J.; Periyasamy, S. Extraction and characterization of waste plastic pyrolysis oil for diesel engines. *J. Clean. Prod.* **2022**, *336*, No. 132924.
- (22) Lešnik, L.; Palomar-Torres, A.; Torres-Jiménez, E.; Mata, C.; Volmajer Valh, J.; Kevorkijan, L.; Biluš, I. The effect of HDPE and LDPE pyrolytic oils on cavitation formation in a common-rail diesel injector. *Fuel* **2022**, *330*, No. 125581.
- (23) Kalargaris, I.; Tian, G.; Gu, S. The utilisation of oils produced from plastic waste at different pyrolysis temperatures in a DI diesel engine. *Energy* **2017**, *131*, 179–185.
- (24) Arnold, M.; Boghosian, B.; Li, M. Catalytic production of diesel-like oils from plastic wastes. *J. Renewable Sustainable Energy* **2021**, *13* (6), No. 064701.
- (25) Uttamprakrom; Reubroycharoen, P.; Vitidsant, T.; Charusiri, W. Catalytic degradation of rapeseed (*Brassica napus*) oil to a biofuel using MgO: an optimization and kinetic study. *J. Jpn. Inst. Energy* **2017**, *96* (6), 190–198.
- (26) Chaihad, N.; Anniwaer, A.; Karnjanakom, S.; Kasai, Y.; Kongparakul, S.; Samart, C.; Reubroycharoen, P.; Abudula, A.; Guan, G. In-situ catalytic upgrading of bio-oil derived from fast pyrolysis of sunflower stalk to aromatic hydrocarbons over bifunctional Cu-loaded HZSM-5. *J. Anal. Appl. Pyrolysis* **2021**, *155*, No. 105079.
- (27) Chaihad, N.; Anniwaer, A.; Zahra, A. C. A.; Kasai, Y.; Reubroycharoen, R.; Kusakabe, K.; Abudula, A.; Guan, G. In-situ catalytic upgrading of bio-oil from rapid pyrolysis of biomass over hollow HZSM-5 with mesoporous shell. *Bioresour. Technol.* **2021**, *321*, 845–874.
- (28) Charusiri, W.; Phowan, N.; Vitidsant, T. Catalytic copyrolysis of sugarcane leaves and low-density polyethylene waste of product bio-oil and chemicals using Copper-doped ZSM-35. *Energy Fuels* **2022**, *36*, 2639–2655.

- (29) Sambandam, P.; Venu, H.; Narayanaperumal, B. K. Effective utilization and evaluation of waste plastic pyrolysis oil in a low heat rejection single cylinder diesel engine. *Energy Sources, Part A* **2020**.
- (30) Padmanabhan, S.; Giridharan, K.; Stalin, B.; Kumaran, S.; Kavimani, V.; Nagaprasad, N.; Jule, L. T.; Krishnaraj, R. Energy recovery of waste plastics into diesel fuel with ethanol and ethoxy ethyl acetate additives on circular economy strategy. *Sci. Rep.* **2022**, *12*, 5330.
- (31) Tulashie, S. K.; Doodoo, D.; Mensah, S.; Atisey, S.; Odai, R.; Adukpoh, K. E.; Boadu, E. K. Recycling of plastic wastes into alternative fuels towards a circular economy in Ghana. *Clean. Chem. Eng.* **2022**, *4*, No. 100064.
- (32) Wang, Y.; Dai, L.; Fan, L.; Cao, L.; Zhou, Y.; Zhao, Y.; Liu, Y.; Ruan, R. Catalytic copyrolysis of waste vegetable oil and high-density polyethylene for hydrocarbon fuel production. *J. Waste Manage.* **2017**, *61*, 276–282.
- (33) Charusiri, W.; Phowan, N.; Vitidsant, T. Pyrolysis of lignocellulosic biomass with high density polyethylene to produce chemicals and bio-oil with high liquid yields. *Sustainable Chem. Pharm.* **2022**, *25*, No. 100567.
- (34) Huo, E.; Lei, H.; Liu, C.; Zhang, Y.; Xin, L.; Zhao, Y.; Qian, M.; Zhang, Q.; Lin, X.; Wang, C.; Mateo, W.; Villota, E. M.; Ruan, R. Jet fuel and hydrocarbon produced from waste plastics catalytic pyrolysis with activated carbon and MgO. *Sci. Total Environ.* **2020**, *727*, No. 138411.
- (35) Zhang, Y.; Duan, D.; Lei, H.; Villota, E.; Ruan, R. Jet fuel production from waste plastics via catalytic pyrolysis with activated carbons. *Appl. Energy* **2019**, *251*, No. 113337.
- (36) Junzhi, W.; Xiaowen, Q.; Xinjiang, D.; Siyi, L.; Yu, F.; Mao, F. The co-pyrolysis of waste tires and waste engine oil. *Energy Source, Part A* **2022**, *44* (4), 9764–9778.
- (37) Banchapattanasakda, W.; Asavatessanupap, C.; Santikunaporn, M. Conversion of waste cooking oil into bio-fuel via pyrolysis using activated carbon as catalyst. *Molecules* **2023**, *28* (8), 3590.
- (38) Hasan, M. M.; Rasul, M. G.; Jahirul, M. I.; Khan, M. M. K. Characterization of pyrolysis oil produced from organic and plastic wastes using an auger reactor. *Energy Convers. Manage.* **2023**, *278*, No. 116723.
- (39) Yue, L.; Li, G.; He, G.; Guo, Y.; Xu, L.; Fang, W. Impacts of hydrogen to carbon ratio (H/C) on fundamental properties and supercritical cracking performance of hydrocarbon fuels. *Chem. Eng. J.* **2016**, *283*, 1216–1223.
- (40) Dangdara, P.; Subsadsana, M.; Ruangviriyachai, C. Liquid biofuel production from palm oil using dual-function of Zn/HZSM-5 catalyst. *Orient. J. Chem.* **2017**, *33* (5), 2257–2262.
- (41) Gouda, N.; Panda, A.; Singh, R. K.; Ratha, S. K. Pyrolytic conversion of protein rich microalgae *Arthrospira platensis* to bio-oil. *Res. J. Chem. Environ.* **2018**, *22*, 54–65.
- (42) Li, L.; Yan, B.; Li, H.; Yu, S.; Ge, X. Decreasing the acid value of pyrolysis oil via esterification using ZrO₂/SBA-15 as a solid acid catalyst. *Renewable Energy* **2020**, *146*, 643–650.