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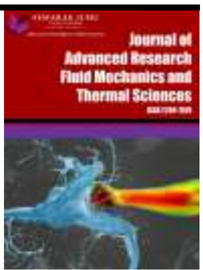

Catalytic Co-Pyrolysis of Oil Palm Frond and Plastic Waste into Liquid Fuel using Ni-CaO Catalyst

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ABSTRACT

The decline in fossil fuel sources is directly linked to the increasing global energy demand, highlighting the urgent need for renewable energy sources. One highly efficient and eco-friendly alternative is bio-oil from co-pyrolysis, a process that effectively breaks down biomass with a high hydrogen index efficiency ratio (H/C). This research comprehensively examines the factors influencing bio-oil production, including the pretreatment of palm fronds with formic acid, the ratio of plastic to palm frond, and the percentage of Ni-CaO catalysts. The study reveals that pretreating the biomass with formic acid and adding low-density polyethylene (LDPE) plastic increase bio-oil yield, while the addition of Ni-CaO catalyst has the opposite effect. These variations notably impact the enhancement of bio-oil quality, as evidenced by calorific value, acid number, density, and bio-oil constituent compounds. Specifically, Bio-oil obtained from OPF prepared with 70% formic acid, 50:50 OPF to LDPE ratio and 15% Ni-CaO catalyst addition yielded 49.6% with an acid number of 8.57 mgKOH/g, density of 0.98 g/mL and heating value of 31.732 MJ/Kg.

1. Introduction

The demand and consumption of fossil fuels in the world have increased dramatically, leading to serious environmental problems such as greenhouse gas and sulfur oxide emissions [1]. Fossil fuels are the world's main source of energy, the combustion products of which are generally the main source of pollutants, such as SO_2, NO_x, CO, and CO_2 [2]. Greenhouse gases produced from fossil fuels can cause climate change [3]. Increasing global energy demand and depleting fuel reserves are forcing us to study renewable and environmentally friendly energy sources [4].

One of the renewable energy sources is biomass. This material is abundant and easily available, especially in areas with high agricultural activity. Indonesia has 10.5 million hectares of oil palm plantations that can produce 10.4 tons of oil palm fronds (OPF) per hectare per year. So far, the utilization of oil palm fronds has not been optimal; they are only used for composting, animal feed, and the rest as waste [4]. Whereas OPF has greater potential to be utilized as bio-oil because it

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contains high levels of cellulose, hemicellulose, and lignin. Palm fronds consist of lignocellulosic components, such as 45.22% cellulose, 19.22% hemicellulose, 31.24% lignin, and 4.32% extractive substances [5].

Pyrolysis is a very promising process to convert biomass into bio-oil, bio-char, and non-condensable gases. This process usually occurs at high temperatures and in the absence of oxygen [6]. While pyrolytic oil produced from pyrolysis is a promising alternative fuel, its use as a liquid fuel is very limited due to its high oxygen content, high viscosity, corrosion, and thermal instability. The high oxygen content in pyrolytic oil gives it a low heating value [7]. To reduce these problems, the quality of bio-oil needs to be improved. Co-pyrolysis is a recent technique used to improve bio-oil quality by mixing biomass with synthetic polymers [3].

The effect of plastic with biomass during co-pyrolysis has a positive effect because plastic is a polymer product with a high hydrocarbon composition, and the liquid product produced from plastic pyrolysis has a heating value close to the heating value of conventional fuels, which is about 40 MJ/kg [8]. Low-density polyethylene is a plastic rich in hydrogen content, which is 15.40%. Pyrolysis of plastics produces liquid products with a predominance of hydrocarbon compounds and low oxygenate compounds, so that the oil products have a high heating value and low acidity [9]. Co-pyrolysis of oxygen-rich biomass with hydrogen-rich plastics leads to a synergistic improvement in bio-oil quality with a low O/C ratio and a high H/C ratio [8]. In addition to co-pyrolysis, improving the quality of bio-oil can be done by treating the biomass [10].

Biomass pretreatment is one of the main steps in the thermochemical process that can homogenize and improve biomass characteristics [11]. Pretreatment methods include thermal, chemical, and biological methods [12]. One of the suitable pretreatments for lignocellulosic materials is acid pretreatment, or acid leaching. Acid leaching of biomass can remove minerals from biomass, such as alkali and alkaline earth metals (AAEMs). The removal of AAEMs can improve the yield and quality of bio-oil in biomass pyrolysis [13]. AAEMs reduce hydrocarbon yield in the catalytic pyrolysis of biomass, leading to fewer aromatics and olefins [14]. Besides removing AAEMs, acid pretreatment can reduce lignin in biomass. Lignin acts as a barrier that can prevent cellulose and hemicellulose degradation [15]. Lignin also reduces the yield of levoglucosan from cellulose because phenol derivatives of lignin radicals bind to hydrogen from levoglucosan. While levoglucosan can be converted into aromatic hydrocarbons [16].

Another method to improve the quality of pyrolytic oil is to use catalysts in the pyrolysis process [7]. The use of solid catalysts has attracted much attention in recent years [17]. The catalysts commonly used in the pyrolysis process are HUSY, Hbeta, Zeolite Y, ZSM-5, and Ni/Al_2O_3. These catalysts are able to improve the quality of bio-oil. However, due to the high cost and limited availability of synthesis, the use of natural catalysts such as calcium oxide is an appropriate method. Due to its environmental friendliness and low cost, CaO was studied as a catalyst for bio-oil quality improvement [18]. CaO catalyst has a strong alkali that facilitates oxygen removal by removing carboxylic acids and phenols and increasing hydrocarbons from bio-oil products [19]. Therefore, co-pyrolysis of OPF and LDPE plastic using Ni-CaO catalyst was conducted in this study. OPF was pretreated with formic acid which is an environmentally friendly acid. OPF pretreatment and the use of Ni-CaO catalyst were able to improve the quality of bio-oil as a co-pyrolysis product.

2. Methodology

2.1 Material and Instruments

The materials used were oil palm fronds (OPF), low-density polyethylene (LDPE), formic acid, hydrochloric acid, nitrogen, nickel nitrate hexahydrate, and calcium hydroxide. The tools used were an oven, an analytical balance, a condenser, a pyrolysis reactor, a temperature regulator, a stative and clamp, an N_2 gas cylinder and regulator, a thermocouple, a 1000-ml beaker, a 10-ml measuring cup, a 250-ml Erlenmeyer round measuring cup, scissors, a drop pipette, a pH meter, and a bio-oil sample bottle. Figure 1 is a circuit of the co-pyrolysis apparatus.

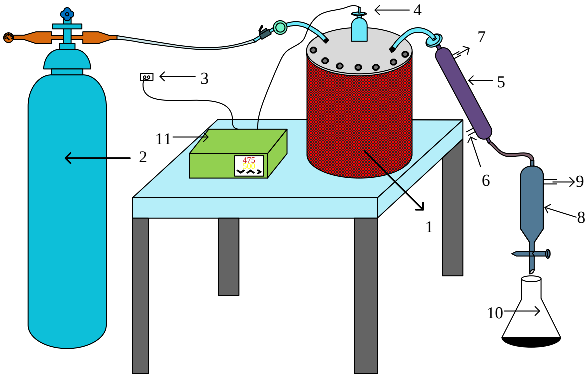

Fig. 1. Schematic diagram of the experimental for co-pyrolysis. (1) pyrolysis reactor; (2) nitrogen cylinder; (3) power source; (4) temperature sensor (5)-condenser; (6)-input of cooling water; (7) output of cooling water; (8) separator; (9) output of non-condensable gas; (10) Erlenmeyer; and (11) temperature controller

2.2 Raw Materials Preparation

Palm fronds obtained from the Faculty of Agriculture at Riau University were cut to a certain size and then dried in the sun. The dried palm fronds were measured for moisture content and then pretreated with formic acid with various concentrations of 0%, 60%, 70%, 80%, and 90% at 105 oC for 1.5 hours. Then the pretreatment results were filtered and washed with a neutral pH, then dried in an oven at 110 oC until a constant weight was reached. LDPE plastic waste was cleaned and then cut into specific sizes.

2.3 Pyrolysis and Co-pyrolysis

Each treated biomass was pyrolyzed at 500^{o}C. For the co-pyrolysis process, OPF and LDPE plastic raw materials were mixed with ratios of 0/100, 25/75, 40/60, 50/50, 75/25, and 100/0 and heated at 500^{o}C. For catalytic co-pyrolysis of OPF/LDPE (50:50), Ni-CaO catalyst was added with a ratio of catalyst to the feedstock of 0%, 5%, 10%, 15%, and 20% and operated at 500^{o}C. The liquid product (bio-oil) was collected and weighed to measure the yield. The bio-oil composition was analyzed by GC-MS. Bio-oil characteristics were measured by bomb calorimetry, acid number, pH meter, and pycnometer.

3. Results

3.1 Physical and Chemical Analysis of Catalyst Ni-CaO

In this study, CaO catalyst doped with nickel (Ni) was used. The expected ratio of Ni in the CaO catalyst is 5%wt. The preparation of the Ni-CaO catalyst in this study used the wet impregnation method.Based on the morphological structure shown in Figure 2 below, it can be seen that, with a magnification of 5000 times, the surface of the resulting Ni-CaO catalyst forms particles of irregular sizes. According to Scaccia *et al.,* [20], the surface of the Ni-CaO catalyst consists of slab-shaped particles with irregular sizes (0.1–1 m) that overlap each other in an inhomogeneous layer resembling rosette morphology. Asikin-Mijan *et al.,* [21] stated that the Ni-CaO catalyst has an irregular cube-like structure and a large particle size.

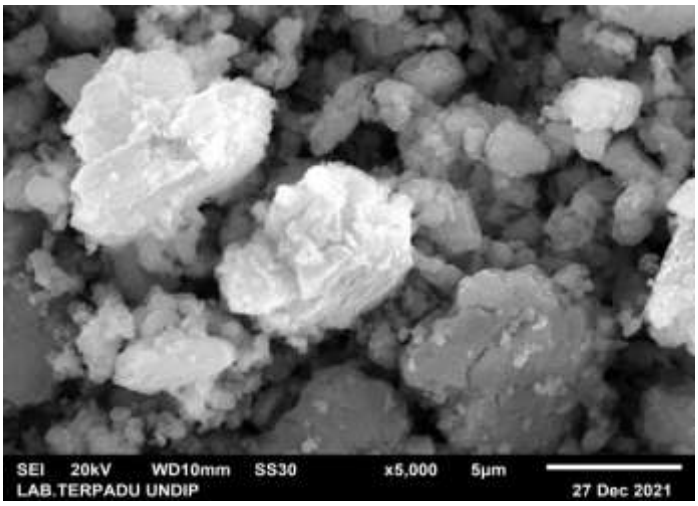

Fig. 2. SEM image of catalyst Ni-CaO 5000x magnification

The Ni-CaO catalyst was also analyzed by EDX, which is an energy dispersion detector, so that it can be used to determine the elemental composition present in the catalyst sample. In Table 1 below, it can be seen that the EDX results on the Ni-CaO catalyst have a metal composition of Ni reaching 5.84%. In the Ni-CaO catalyst, there are carbon atoms (C) of as much as 22.96%. The carbon atoms detected in this catalyst come from CaCO3 compounds that do not decompose into CO2 in the calcination process. Amzah [22] conducted research on the manufacture of Ni-CaO catalysts with the doping method, and there were 29.75% carbon atoms.

Table 1
EDX result of Ni-CaO catalyst

Component	Result of Analysis (% w/w)
C (balance)	22.96
MgO	0.63
CaO	67.87
NiO	5.84
CuO	2.70

In Table 1, it can be seen that the Ni-CaO catalyst contains 2.70% CuO. Asikin-Mijan *et al.,* [21] stated that the synthesized CaO catalyst contains 1.19% CuO. The presence of CuO does not have a bad influence on the Ni-CaO catalyst. According to Sonobe *et al.,* [23] the presence of CuO compounds on the catalyst can provide a good synergistic role as a catalyst. This is because CuO chemical compounds are stable in the form of metal oxides that have strong bases and are active in the form of lone electron pairs so as to increase the reactivity of metal oxide compounds as catalysts.

Table 2 shows that the Ni-CaO catalyst in this study has a larger surface area and pore volume compared to the catalyst produced by Amzah [22]. When compared with CaO catalysts, the surface area of Ni-CaO catalysts is smaller, while the pore volume and radius are larger. The area of the CaO catalyst will decrease with the addition of nickel content to the catalyst [24]. The large pore size of the Ni-CaO catalyst is caused by the collapse of the CaO pore wall during the impregnation process or defects in the CaO structure [25].

Table 2
BET analysis result of Ni-CaO catalyst

Parameter	Ni-CaO This research	Ni-CaO [22]	CaO [24]
Surface Area	16.251 m^2/g	15.011 m^2/gr	21.1 m^2/g
Pore Radius	134.171 Å	161.230 Å	19.6 Å
Pore Volum	0.105 cc/g	0.054 cc/g	0.12 cc/g

3.2 Analysis of the Influence of Formic Acid Concentration on the Pretreatment Process of Oil Palm Frond on Bio-Oil Yield

Pretreatment of oil palm frond (OPF) was carried out physically and chemically. Physical pretreatment was carried out by reducing the palm frond size to 2 cm and drying it under the sun. Chemical pretreatment of OPF was carried out by the delignification method using formic acid (FA) as a leaching agent with concentration variations of 60%, 70%, 80%, and 90%. According to Bensah and Mensah [26], formic acid is a compound that has good solubility in lignin, and the process can be carried out at low temperatures and atmospheric pressures. In addition, acid leaching of biomass can remove minerals from biomass, namely alkali and alkaline earth metals (AAEMs), thereby promoting an increase in bio-oil yield and improving bio-oil quality [13]. Figure 3 shows the effect of formic acid concentration on OPF pretreatment on lignocellulose composition.

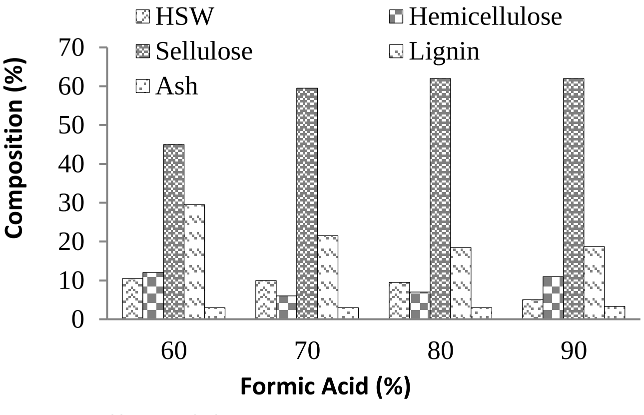

Fig. 3. Effect of formic acid concentration on palm frond pretreatment on lignocellulosic composition

In Figure 3, it can be seen that as the concentration of formic acid increases, the lignin content in OPF decreases. Increasing the concentration of formic acid causes an increase in the degree of delignification, so that more lignin is successfully removed and dissolved in the solvent. Formic acid causes the hydrolysis of ether bonds in lignin so that lignin dissolves in black liquor. Formic acid also causes the decomposition of hemicellulose through glycosidic hydrolysis, producing oligomers and sugar monomers, which are both soluble in the liquid phase, so that hemicellulose is reduced in OPF [27].

Table 3 shows the results of the proximate analysis of OPF that has been pretreated with 70% formic acid and OPF in other studies. Based on Table 3, it can be seen that with 70% formic acid pretreatment, the volatile matter content of oil palm fronds is higher. Pyrolysis feedstock is expected to contain highly volatile matter. According to Palamanit *et al.,* [28], volatile matter is an important component of biomass to produce bio-oil or liquid products. In addition, Kabir *et al.,* [5] stated that biomass with a high volatile matter fraction is reactive during the pyrolysis process, resulting in high bio-oil and gas yields.

Table 3
Results of proximate and ultimate analysis of oil palm frond

Parameter	OPF Pretreatment 70 % FA	Palamanit *et al.,* [28]	Kabir *et al.,* [5]	Umar *et al.,* [29]
Proximate				
Moisture (%)	9.29	7.50	4.83	1.9
Volatile Matter (%)	77.74	73.06	70.33	66.10
Fixed Carbon (%)	11.1	16.55	18.97	25.68
Ash Content (%)	1.87	2.89	5.87	6.32
Ultimate				
Carbon (%)	43.95	43.45	41	45.42
Hydrogen (%)	6.40	6.08	6.74	6.35
Nitrogen (%)	0.34	0.19	0.67	0.47
Sulfur (%)	0.10	0.01	0.35	0.13
Oxygen (%)	47.89	50.28	51.24	47.63

In Table 3, the fixed carbon and ash content of palm fronds decreased after pretreatment with 70% formic acid. According to Palamanit *et al.,* [28], the fixed carbon content in biomass cannot be converted into bio-oil but is converted into charcoal. Ash is the inorganic content of biomass. Biomass with high ash content is not suitable for bio-oil production through pyrolysis because it causes low bio-oil yields.

Table 3 shows the results of the ultimate analysis of palm fronds that have been prepared with 70% formic acid and palm fronds in other studies. The content of carbon (C) and hydrogen (H) in the OPF of this study is higher than that of Palamanit *et al.,* [28]. Biomass with high C and H content provides a high heating value. For the pyrolysis process, biomass with a high carbon and hydrogen content is preferred. This is because C and H can be converted into aromatic compounds in bio-oil products.

The oxygen content in this study is lower than that in the studies of Palamanit *et al.,* [28] and Kabir *et al.,* [5]. Biomass with low oxygen content produces low oxygenate compounds in the pyrolysis process. Low oxygen content also produces bio-oil with low water content.

The sulfur and nitrogen contents of the raw materials in this study were lower than those of Kabir *et al.,* [5] and Umar *et al.,* [29]. According to Palamanit *et al.,* [28], the lower the nitrogen and sulfur content, the less SOx and NOx are formed in the pyrolysis process.

The pyrolysis process was carried out at a temperature of 500^{o}C using raw material from OPF that had been physically and chemically pretreated. The effect of formic acid concentration on bio-oil yield can be seen in Figure 4.

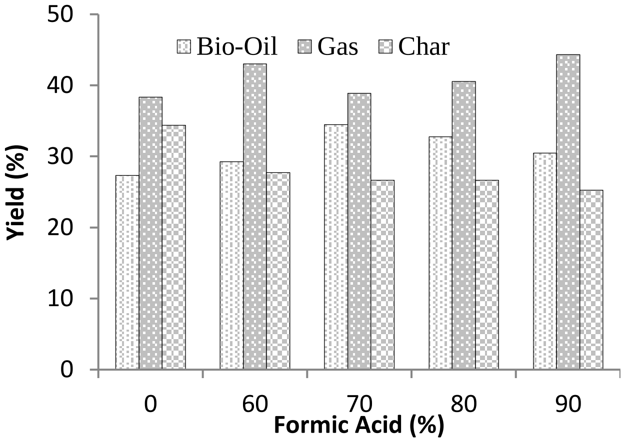

Fig. 4. Effect of formic acid concentration on pretreatment of OPF on yield of products

Figure 4 shows that the bio-oil yield increased with increasing formic acid concentration. With OPF pretreatment using 0%, 60%, and 70% formic acid, the bio-oil yield increased to 27.30%, 29.27%, and 34.47%, respectively. However, at 80% and 90% formic acid percentages, the bio-oil yield slightly decreased to 32.77% and 30.45%, respectively. This increase in bio-oil yield shows the positive effect of reducing the lignin and hemicellulose content of the feedstock through the delignification process.

The increase in bio-oil yield at 0%, 60%, and 70% formic acid concentrations is in line with the increase in cellulose composition in the feedstock, which can be seen in Figure 3. The decrease in bio-oil yield at 80% and 90% formic acid concentrations is due to the increase in lignin.

Thermal decomposition of hemicellulose is in the temperature range of 220-350°C, while cellulose is in the temperature range of 325-400°C, so pyrolysis at 500°C produces more gas products. In addition, Hong and Wang [30] stated that the bio-oil yield is higher for cellulose pyrolysis than hemicellulose and lignin, which produce more char and gas.

3.3 Analysis of the Effect of Raw Material Ratio on Yield Bio-Oil

The co-pyrolysis process using OPF and Low-Density Polyethylene (LDPE) as raw materials with ratios of 100/0, 75/25, 60/40, 50/50, 25/75, and 0/100 was carried out at 500°C. Based on pretreatment using formic acid, bio-oil was obtained with the best characteristics at 70% formic acid concentration. So the OPF that has been pretreated with 70% formic acid was selected as the raw material to be used in the co-pyrolysis process. The results of the effect of the ratio of raw materials on the yield of the resulting bio-oil can be seen in Figure 5.

Figure 5 shows that the bio-oil yield increases at 75/25, 60/40, and 50/50, but the bio-oil yield decreases starting at 25/75 and 0/100. This result shows the same trend as the research conducted by Dewangan *et al.,* [8]. At the ratio between bagasse and LDPE of 9/1, 3/1, and 1/1, the bio-oil yield increased to 39.5%, 42%, and 52.75%, respectively. However, in the 1/3 ratio, the bio-oil yield decreased to 45%.

The increase in liquid product yield is due to the hydrogen donor from polyethylene during co-pyrolysis. In the co-pyrolysis process, several radical reactions occur, such as initiation, secondary radical formation through depolymerization, monomer formation, hydrogen transfer, isomerization, and termination through disproportionation or radical recombination [8]. However, the high volatile matter content in LDPE makes it possible to form gaseous products in the co-pyrolysis process. Figure 5 shows that the OPF:LDPE ratio of 25:75 and 0:100 decreased the bio-oil yield by 32.46% and 24.7%, respectively, while the gas yield increased by 60.68% and 75.3%.

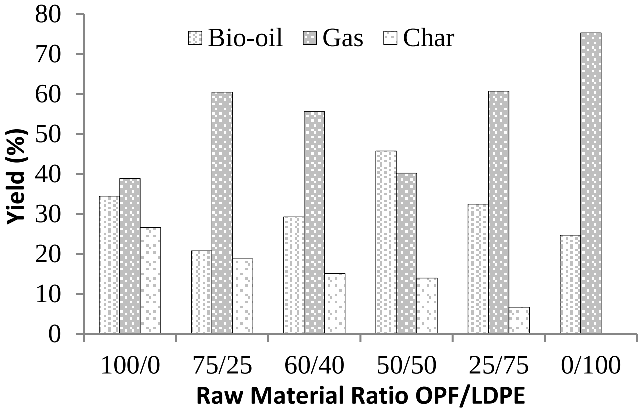

Fig. 5. Effect of raw material ratio on product yield

3.4 Analysis of the Effect of the Addition of Ni-CaO Catalyst on Yield Bio-oil

In this study, the co-pyrolysis of oil palm fronds and LDPE was carried out using a percentage of Ni-CaO catalyst of 5% w/w, 10% w/w, 15% w/w, and 20% w/w with a ratio of treated OPF and LDPE of 50/50. The effect of the weight ratio of the Ni-CaO catalyst on the yield of bio-oil produced can be seen in Figure 6.

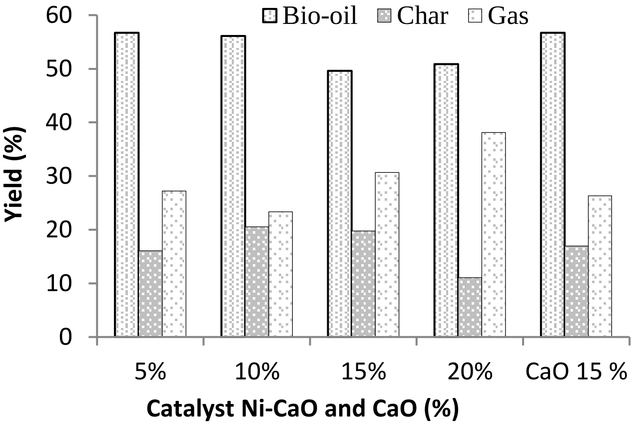

Fig. 6. Effect of addition of Ni-CaO and CaO catalysts on yield of bio-oil, gas and char

In Figure 6, it can be seen that the yield of bio-oil decreased with the addition of a Ni-CaO catalyst. With the addition of 5%, 10%, 15%, and 20% catalyst to the mass of raw material the yield of bio-oil obtained decreased by 56.72%, 56.12%, 49.6%, and 50.84%. According to Xu *et al.,* [31], the addition of Ni to the CaO catalyst promotes the decomposition of organic macromolecules and the formation of gaseous products so that the use of a Ni-CaO catalyst not only increases the gas composition and calorific value but also reduces the amount of liquid.

In Figure 6, it can be seen that the yield ratio of bio-oil with 15% Ni-CaO and 15% CaO catalyst can be seen, the yield with Catalyst CaO reaches 56.72% while that with Catalyst Ni-CaO is only 49.6%. According to Xu *et al.,* [31], Ni-CaO catalyst has better cracking catalytic ability than CaO catalyst alone, so the use of Ni-CaO catalyst produces lighter compounds. This is evidenced by the composition of Ni-CaO gas which is higher than gas with CaO catalyst.

3.5 Effect of Biomass Pretreatment on Physical Properties of Bio-oil

Characterization analysis of bio-oil was carried out to determine some important physical properties for fuel requirements such as density, acid number, pH, and calorific value. Table 4 shows the physical properties of the pyrolytic oil produced in this study.

Table 4
Results of characterization of physical properties of bio-oil on the effect of biomass pretreatment

Formic Acid (%)	Density (g/mL)	Acid Number (mg KOH/g)	pH
0	1.011	167.51	2.5
60	0.935	121.71	2.8
70	1.092	78.26	3.4
80	1.085	77.26	3.4
90	1.099	76.79	3.6

From Table 4, the bio-oil density value for each variation of formic acid concentration did not show a significant change with the highest value of 1.099 g/mL and the lowest value of 0.935 g/mL, the bio-oil density value for each variation of formic acid concentration was still in the range of standard values of bio-oil density is 0.9-1.2 g/mL.

Table 4 shows the value of the bio-oil acid number for each variation of formic acid concentration, it can be seen for variations in the concentration of formic acid 0%, 60%, and 70% showing a very significant decrease in acid number, namely 167.51 mg KOH/g, 121 .71 mg KOH/g and 78.26 mg KOH/g, while for variations of 70%, 80% and 90% the value of the acid number still decreased but was not so significant, namely 78.26 mg KOH/g, 77.26 mg KOH/g and 76.79 mg KOH/g.

In Table 4, it can be seen the value of the pH of the bio-oil for each variation in the concentration of formic acid. For variations in the concentration of 0% and 60% of the pH of bio-oil, respectively, are 2.5 and 2.8, this value is still included in the standard range of pH values for bio-oil, which is 2-3. For variations of 70%, 80%, and 90%, the pH values of bio-oil are 3.4, 3.4, and 3.6, respectively, indicating an increase in quality compared to standard bio-oil. According to Yu *et al.,* [32], bio-oil has a low pH due to its high organic acid content (acetic acid and formic acid). In another study, according to Lu *et al.,* [33], carboxylic acids cause the low pH of the bio-oil.

In Figure 3, it can be seen that with an increase in the concentration of formic acid, the composition of lignin and hemicellulose tends to decrease, this decrease in the composition of lignin and hemicellulose has a positive effect on the decreasing value of acid number and increasing pH. According to Solikhah *et al.,* [4] decomposition of lignin and hemicellulose form acidic compounds. So that the reduced composition of hemicellulose and lignin causes fewer acid compounds to be formed.

3.6 Effect of Raw Material Ratio on Physical Properties of Bio-oil

Characterization analysis of bio-oil was carried out to determine some important physical properties for fuel requirements such as density, acid number, pH, and calorific value. In Table 5 and Table 6 can be seen the physical properties of the bio-oil produced in this study.

From Table 5, bio-oil density values for each variation of the raw material ratio with the highest value of 1.09 g/mL and the lowest value of 0.78 g/mL, the value of bio-oil density for each variation of the ratio of raw materials LDPE: PF 0/100, 25/75, 40/60, and 50/50 are still in the range of standard bio-oil density values, namely 0.9-1.2 g/mL, while for variations 75/25, and 100/0 the density values are 0.78 g/mL. The results of this study are in accordance with those stated by Sunarno *et al.,* [9]. The pyrolytic density of the oil decreases with increasing plastic ratio in the feedstock. Bio-oil in each variation has a density higher than the density of diesel oil 0.85 g/mL, this indicates a positive nature. In the pyrolysis of OPF, the density of bio-oil was higher than that of co-pyrolysis of palm fronds and polyethylene. According to Thoharudin *et al.,* [7], Bio-oil with a higher density has a higher content of oxygenated compounds, this is because oxygen has a higher atomic mass.

In Table 5, it can be seen the value of the acid number for each variation of the ratio of raw materials. For all variations of the ratio of polyethylene to palm fronds 0/100, 25/75, 40/60, 50/50, and 75/25, the acid number values were 70.18, 67.43, 63.37, 64.9, and 2.95 mgKOH/g. From the overall data, it can be seen that there is a decrease in the acid number for each increase in the polyethylene ratio.

Table 5 shows the value of the pH of bio-oil for each variation of the ratio of polyethylene raw materials and palm fronds. For the variation of polyethylene against oil palm fronds 0/100, 25/75, 40/60, 50/50, 75/25, and 100/0 the pH value for each bio-oil was 3.4; 5.2; 5,6; 5.5; 4.2; 4.8. For all variations of the pH value of the bio-oil produced, it is above the standard bio-oil pH value of 2-3, for variations of 25/75, 40/60, and 50/50, the pH value has reached the Diesel Oil pH of 5. Co-pyrolysis plastic and biomass showed a positive synergistic effect resulting in pyrolysis oil with a higher pH.

Table 5
Results of the characterization of physical properties of bio-oil on the effect of raw material ratio

Raw Material (LDPE:OPF)	Density (g/mL)	Acid Number (mg KOH/ g)	pH
0/100	1.09	70.18	3.4
25:75	1.00	67.43	5.2
40:60	0.95	63.37	5.6
50:50	0.95	64.9	5.5
75:25	0.78	2.95	4.2
100:0	0.78	-	4.8

The calorific value for each variation of the ratio of raw materials can be seen in Table 6. The calorific value increased with the addition of the amount of polyethylene plastic. In the variation of the ratio of polyethylene raw materials to palm fronds 100/0, 75/25, 50/50, 40/60, and 25/75, the calorific value is 51.934 MJ/kg, 48.904 MJ/kg, 27.252 MJ/kg, 5.6 MJ/kg, and 2.165 MJ/kg. For the variation of polyethylene raw material on OPF 100/0 and 75/25, the calorific value has reached the calorific value of diesel oil, which is 42.75 MJ/kg. For the variation of polyethylene raw material on palm fronds 1:1, the calorific value is above the standard calorific value range of bio-oil, namely 13 MJ/kg–19 MJ/kg, but has not yet reached the calorific value of diesel oil, while for variations of 40/60 and 25/75, the value is still below the standard bio-oil.

The results of this study indicate an increase in the calorific value with the addition of the ratio of plastic to the raw material. According to Dewangan *et al.,* [8]. The content of hydrocarbons (H/C) and oxygen content play an important role in controlling the calorific value of the oil, The increase in calorific value is evident with an increase in the ratio (H/C) through the addition of low-density polyethylene.

Table 6
Results of testing the calorific value of bio-oil on the effect of raw material ratio

No.	Sample (LDPE/OPF)	Calorific Value (MJ/kg)
1.	100/0	51.934
2.	75/25	48.904
3.	50/50	27.252
4.	40/60	5.600
5.	25/75	2.165

3.7 Effect of Addition of Ni-CaO Catalyst on Physical Properties of Bio-oil

Characterization analysis of bio-oil was carried out to determine some important physical properties for fuel requirements such as density, acid number, pH, and calorific value. In Table 7 and Table 8 can be seen the physical properties of the bio-oil produced in this study.

From Table 7, the value of the density of bio-oil for each variation in the percentage of catalyst did not show a significant change with the highest value of 1.02 g/mL and the lowest value of 0.94 g/mL, the value of density of bio-oil for each variation of the percentage of catalyst was still at in the range of standard bio-oil density values of 0.9-1.2 g/mL. Bio-oil in each variation has a density higher than the density of diesel oil 0.85 g/mL, which indicates a positive nature.

The density value of bio-oil produced for each variation did not show a significant change; this was in accordance with what was stated by Thoharudin *et al.,* [7]. The addition of a catalyst can causes the cracking of heavy hydrocarbons into lighter hydrocarbons with a lighter density, but this is offset by a neutralization reaction by the catalyst, which produces water with a high density.

From Table 7, it can be seen that with the increase in the amount of Ni-CaO catalyst used, the acid number of bio-oil also decreases. At the percentages of 0%, 5%, 10%, 15%, and 20%, the acid number values were 64.9 mg KOH/g, 46.82 mg KOH/g, 15.75 mg KOH/g, 8.57 mg KOH/g, and 4.33. This decrease in the value of the acid number indicates an increase in the quality of the bio-oil produced. According to Zhang *et al.,* [17], CaO has strong basicity to facilitate the removal of oxygen by eliminating carboxylic acids and phenols from bio-oil. According to Vichaphund *et al.,* [25], the decrease in acid levels and oxygenate compounds, as well as an increase in hydrocarbon compounds in the presence of a Ni-CaO catalyst, occurs through decarboxylation, decarbonylation, denitrogenation, and cracking reactions. Furthermore, the presence of Ni metal encourages the cracking of lignin-derived compounds, thereby reducing the phenol content.

Table 7
Results of characterization of physical properties of bio-oil on the effect of addition of catalyst Ni-CaO

Percentage of Catalyst	Density (g/mL)	Acid Number (mg KOH/ g)
0	0.95	64.9
5%	1.02	46.82
10%	0.94	15.75
15%	0.98	8.57
20%	0.97	4.33

The calorific value for each percent variation of Ni-CaO catalyst against raw materials can be seen in Table 8. The calorific value increased with the addition of a 15% Ni-CaO catalyst. In the percentage variation of the catalyst to the raw material at 5%, 10%, 15%, and 20%, the calorific value is 29.791 MJ/kg, 30.985 MJ/kg, 31.732 MJ/kg, and 30.985 MJ/kg. For all variations of the Ni-CaO catalyst, the calorific value is above the standard calorific value range of bio-oil, namely 13 MJ/kg–19 MJ/kg, but has not yet reached the calorific value of diesel oil.

Table 8
Results of testing the calorific value of bio-oil on the effect of addition of Ni-CaO catalyst and comparison of CaO catalyst

No.	Sample	Calorific Value (MJ/kg)
1	PE:OPF (1:1) CaO 15 %	29.791
2	PE:OPF (1:1) Ni-CaO 5 %	30.239
3	PE:OPF (1:1) Ni-CaO 10 %	30.985
4	PE:OPF (1:1) Ni-CaO 15 %	31.732
5	PE:OPF (1:1) Ni-CaO 20 %	30.985

In this variable, the CaO catalyst is also used as a comparison for the Ni-CaO catalyst; the heating value for the 15% CaO catalyst is 29.791 MJ/kg, while for the 15% Ni-CaO catalyst, the heating value is higher, namely 31.732 MJ/kg. The calorific value of bio-oil using a Ni-CaO catalyst is higher than that of bio-oil using a CaO catalyst, which indicates that the addition of Ni metal to the CaO catalyst has a positive effect. According to Vichaphund *et al.,* [25], Ni-CaO catalysts are effective for deoxygenation reactions (oxygen release) in the pyrolysis process to improve the quality of bio-oil. Xu *et al.,* [31] stated that Ni-CaO catalyst have better cracking catalytic ability than CaO catalysts, so the use of Ni-CaO catalyst produces lighter compounds.

3.8 Characterization of Chemical Properties of Bio-oil

To determine the components of chemical compounds contained in bio-oil, chemical analysis was carried out using gas chromatography-mass spectrometry (GC-MS). Table 9, Table 10, and Table 11 are the results of the GC-MS test from the best sample results in each variation. The bio-oil produced from this research contains complex organic compounds and hydrocarbons, these compounds are the decomposition of OPF and PE.

Table 9 shows the results of the best sample GC-MS for each variation. The three samples appeared to contain organic compounds and hydrocarbons. The content of hydrocarbon compounds (alkanes and alkenes) for each sample was 70% FA, PE: OPF 1:1, and 15% Ni-CaO obtained at 15.73%, 87.71% (50.67% and 37.04%), and 92.2% (58.58% and 33.62%). In the bio-oil of the 70% FA sample, alkane compounds, namely pentane-3-methyl and cyclopentane, methyl, were found at 3.31% and 12.41%, respectively. In the bio-oil of the PE:OPF 1:1 sample for pentane-3-methyl and cyclopentane, the methyl was 5.93% and 22.47%, respectively. In the bio-oil of the 15% Ni-CaO sample, pentane-3-methyl and cyclopentane were found, with 8.024% and 30.56% methyl, respectively. By comparing the three best samples of each variation, it was shown that the content of pentane-3-methyl and cyclopentane-methyl increased with the addition of plastic and increased with the use of a catalyst. This is similar to the research of Dewangan *et al.,* [8], where the addition of an LPDE increased the hydrocarbon content in bio-oil. The use of plastic causes an increase in the hydrocarbon content, which encourages the increase in pentane-3-methyl and cyclopentane-3-methyl. According to Al-Maari *et al.,* [34], bio-oil derived from plastic is rich in hydrocarbons, as is bio-oil from LPDE, which is plastic. According to Wang *et al.,* [35], CaO has high selectivity toward deacidification and the formation of hydrocarbons. The research of Sunarno *et al.,* [10] showed that the hydrocarbon content increased in the bio-oil as a result of co-pyrolysis of palm shells and LPDE using 20% wt. CaO catalyst compared to no catalyst and tended to increase when using 30% wt. CaO catalyst.

In the PE: OPF 1:1 and 15% Ni-CaO samples, in addition to the discovery of hydrocarbon compounds such as pentane-3-methyl and cyclopentane, there were also several other hydrocarbon compounds found, including several n-alkane compounds such as heptane, octane, nonane, dean, etc. In addition, alkene compounds were also found. The presence of n-alkanes in the C5-C23 range in the bio-oil sample PE:OPF 1:1 was caused by the degradation of polyethylene. According to Sojak *et al.,* [36], thermal cracking of LDPE produces n-alkanes, alk-1-enes, (E)-alk-2-enes, (Z)-alk-2-enes, and alka-α,ω-dienes. In the GC-MS results from the 70% AF bio-oil sample, 21.42% and 78.58% cyclic and aliphatic hydrocarbons were obtained, respectively. On the GC-MS results of the PE:OPF 1:1 bio-oil sample, 36.25% and 63.74% cyclic and aliphatic hydrocarbons were obtained, respectively. Meanwhile, for the 15% Ni-CaO bio-oil sample, 60.01% and 39.99% were obtained. Comparing the three bio-oil samples, there appears to be an increase in aromatic hydrocarbons from the 70% AF sample to the 1:1 PE:OPF sample from 21.42% to 63.74%. There was an increase in the aromatic content of the PE:OPF sample to the 15% Ni-CaO sample from 36.2% to 60.01%. The decrease in oxygenate content (alcohol and esters) from 14.60% in the 1:1 PE:OPF sample to 6.88% in the 15% Ni-CaO sample. CaO catalysts promote the formation of cyclic hydrocarbon compounds in plastic pyrolysis. In a study conducted by Che *et al.,* [37], the addition of CaO to the HZSM-5 catalyst significantly reduced the formation of oxygenate because it has a deoxidizing effect and encourages the formation of aromatics, namely an aromatic increase of 6.14% compared to using HZSM alone. In Che's *et al.,* [37] research, it is also stated that the use of CaO catalysts can increase the formation of benzene, toluene, and xylene. This is following what was obtained in this study, where there was an increase in the benzene content from 0% in the 1:1 OPF:PE sample to 0.18% in the 15% Ni-CaO sample and an increase in toluene from 0% in the OPF:PE 1 sample to 2.22% in the 15% Ni-CaO sample.

The addition of Ni to the catalyst encourages an increase in aromatic hydrocarbons. According to Yung *et al.,* [38], Ni and Sn metals produce the highest aromatics compared to Mg, Cu, and Ga metals. In addition to these metals, research conducted by Shi *et al.,* [39], namely the investigation of the addition of Ni to MCM 41 for the co-pyrolysis of cellulose and propylene. It was found that the addition of Ni as much as 6.9% wt increased the yield of olefin+aromatic from 62.2 to 68.0%, when the Ni was added as much as 25.1% wt, the olefin+aromatic content increased to 84.6%. However, this study conducted by Shi *et al.,* [39] to see the effect of adding nickel also showed that when Ni was added to 25.1% wt., there was a decrease in olefins from 97.3% to 61.2% and an increase in aromatics from 2.7% to 26.6%. This shows that the addition of nickel encourages the formation of aromatics, as in Table 9 there is an increase in aromatics, which also encourages a decrease in olefins. As shown in Table 9, there was a decrease in olefins (alkenes) from 36.93% to 33.52%.

Table 9
Comparison of GC-MS results

COMPOUNDS	%PEAK AREA		
	70%FA	PE:OPF 1:1	15% Ni/CaO
ALKANE	15.80%	50.88%	58.51%
1-DeuteroPropane	-	0.36%	0.13%
Cyclohexane, methyl	-	0.21%	-
Cyclopentane, methyl-	12.41%	22.47%	30.56%
Cyclopropane, nonyl	-	4.44%	3.43%
Decane	-	0.94%	1.11%
Ethane, methoxy-	0.07%	-	-
Heptane	-	0.25%	0.46%
Heptane,2,4 dimethyl	-	0.43%	-
Hexadecane	-	4.17%	5.41%

Nonadecane	-	0.61%	0.55%
Nonane	-	0.69%	0.92%
Octane	-	-	0.60%
Pentacosane -	-	0.29%	-
Pentadecane	-	2.22%	1.90%
Pentane, 3-methyl	3.32%	5.94%	8.02%
Tetradecane	-	2.04%	-
Tridecane	-	4.29%	3.89%
Undecane	-	1.78%	1.53%
ALKENE	-	36.93%	33.52%
(trans)-2-nonadecene	-	0.25%	-
1,10 undecadiene	-	0.21%	-
1,11-dodecadiene	-	0.87%	0.51%
1,9-decadiene	-	0.32%	-
1,9-tetradecadiene	-	0.91%	0.46%
1-decene	-	3.86%	3.47%
1-dodecene	-	4.88%	3.66%
1-heptadecene	-	6.18%	2.31%
1-heptene	-	0.69%	1.06%
1-hexadecene	-	-	2.87%
1-hexene	-	-	0.37%
1-nonadecene	-	3.15%	3.7%
1-nonene	-	2.40%	1.71%
1-octene	-	1.12%	1.29%
1-pentadecene	-	-	3.84%
1-tridecene	-	4.94%	3.29%
3-dodecene	-	0.36%	-
3-undecene	-	-	0.23%
Benzene	-	-	0.18%
Benzene, methyl	-	4.62%	-
Cyclohexene	-	0.14%	0.18%
Cyclopentene, 1-methyl-	-	-	0.27%
Tetradecane	-	-	1.90%
Toluene	-	-	2.22%
Undec-3-ene	-	1.78%	-
ALCOHOL	-	14.60%	6.00%
11-hexadecen-1-ol, (Z)-	-	1.09%	0.78%
E-10-Pentadecenol	-	-	0.46%
1-tridecanol	-	5.31%	-
1-tetradecanol	-	0.83%	3.43%
(R)-(-)-(Z)-14-Methyl-8-hexadecen-1-ol	-	6.28%	1.33%
Carbonothioic acid, O-(1,1-dimethylethyl) S-phenyl ester	-	1.09%	
ESTER	-	-	0.88%
Carbonothioic acid, O-(1,1-dimethylethyl) S-phenyl ester	-	-	0.88%
AMINE	84.10%	-	0.60%
2-Propanamine, 2-methyl-	-	-	0.60%
Methamine, N-Methyl-N-Nitroso	0.08%	-	-
Piperazine	84.02%	-	-
UREA	-	-	0.18%
Urea, N-ethyl-N-nitroso	-		0.18%
AZO	-	-	0.13%
2,3-Diazabicyclo [2.2.1]-hep-2-ene	-	-	0.13%

From Table 10, the 70% FA sample contains 15.73% alkane, while in the PE:OPF 1:1 sample, the alkane content increased to 51.22%. This hydrocarbon product is higher than the product produced by Prasetiawan *et al.,* [40]. This shows that the addition of plastic (LPDE) in co-pyrolysis increases the hydrocarbon content. LPDE is rich in hydrocarbons. In the 15% Ni-CaO sample, the alkane content increased to 58.58%. It shows that the use of a Ni-CaO catalyst increases the alkane content. In addition, the use of a Ni-CaO catalyst reduced the alkene content in the PE:OPF 1:1 sample from 37.05% to 33.63%. The use of a Ni-CaO catalyst also reduces the content of cyclic hydrocarbons when compared to without a catalyst. This is to the research of Kumagai *et al.,* [41], where the use of a CaO catalyst tends to convert complex hydrocarbons into simpler ones by increasing the short-chain hydrocarbons nC2-nC6 and decreasing the content of the longer-chain hydrocarbons nC8-nC17. Allows the conversion of cyclic hydrocarbons to simpler compounds, namely aliphatic. This is also the cause of the decrease in the alkene content.

Table 10
Comparison of GC-MS results

Compound	Composition of Bio-Oil		
	70% FA	PE:OPF 1:1	15%Ni-CaO
Alkane	15.737	50.674	58.581
Alkene		37.049	33.627
Alcohol		13.552	6.029
Esters			0.881
Amine			0.130

From Table 11, the comparison of the GC-MS data from the three samples above shows that bio-oil contains more aliphatic hydrocarbons than cyclic hydrocarbons, as in the study conducted by Dewangan *et al.,* [8]. In the research of Ratnasari *et al.,* [42], namely plastic pyrolysis using HZM-5 and MCM-14 catalysts, the aromatic content of bio-oil produced by pyrolysis using the MCM-14 catalyst was less than that of bio-oil produced by pyrolysis using the HZM-5 catalyst, which was caused by the lower acidity of the MCM-14 catalyst. The Ni-CaO catalyst is an alkaline catalyst that is less acidic than HZSM-5. So using Ni-CaO catalyst tends to increase aliphatic hydrocarbon products.

Table 11
Hydrocarbon content

Hydrocarbon kind	70% AF	PE:OPF 1:1	15%Ni-CaO
Cyclic (%)	21.42	36.25	39.99
Aliphatic (%)	78.58	63.74	60.01

4. Conclusions

The pretreatment of oil palm fronds, the addition of LDPE plastic, and the addition of Ni-CaO catalyst affected the yield of bio-oil produced, the physical properties, and the composition of bio-oil. Increasing the concentration of formic acid to 70% in the palm frond pretreatment process increased the bio-oil yield, but at 80% and 90% concentrations, there was a decrease in bio-oil yield. The addition of plastic with the ratio of palm fronds and plastic 1:1 increased the bio-oil yield, but the addition of Ni-CaO catalyst decreased the bio-oil yield. However, when viewed from the calorific value, pH, acid number, density, and content of bio-oil constituent compounds, all variations showed an increase in bio-oil quality. Bio-oil with optimum conditions in this study was obtained from oil palm fronds prepared with 70% formic acid; the ratio of LDPE to OPF is 1:1, and with the addition of a 15% Ni-CaO catalyst, it had a yield of 49.6%, an acid number of 8.57 mg KOH/g, a density of 0.98 g/mL, and a heating value of 31.732 MJ/kg.

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