



Bio-oil Production from Palm Kernel Cake using fast Pyrolysis Process Parameters in a Fluidized-Bed Reactor

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Abstract

A fast pyrolysis process with a fluidized-bed reactor was investigated for producing bio-oil from palm kernel cake. The process parameters were investigated with the objective of determining the optimal bio-oil yield and properties. Using a biomass particle size of 0.2-0.5 mm, a biomass feed rate of 100 g/h, a carrier gas flow rate of 11 l/min, and a pyrolysis temperature of 550°C resulted in yields of 65.5 wt% total bio-oil, 23.5 wt% char, and 11.0 wt% gas. The total bio-oil yield comprised 47.1 wt% organic bio-oil, 18.4 wt% reaction water, and <1 wt% light bio-oil. As the process conditions varied, the properties of the produced heavy bio-oil changed slightly. Heavy bio-oil had a water content of 6.2-8.7 wt%, a higher heating value of 29.8 MJ/kg, a pH value of 3.5-4.8, a density of 0.94-0.99 kg/dm³, a viscosity of 200 cSt, and a stability of 0.02 cSt/h. These results demonstrated that the characteristics of heavy bio-oil derived from palm kernel cake met the ASTM standards for pyrolysis liquid biofuels.

Keywords: Bio-oil; Fast pyrolysis; Fluidized-bed Reactor; Palm kernel cake.

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1. Introduction

Palm industries generate a significant amount of palm wastes, which can be exploited as valuable raw materials in pyrolysis process. Palm wastes has been pyrolyzed using a variety of reactor designs. For small-scale reactors known as pyrolysis GC/MS (py-GC/MS), many studies^[1-3] used palm wastes

including palm kernel shells, date palm seeds, and palm oil soap, to identify valuable compounds, examine their potential with catalysts, compare them to other wood residues or clarify their thermochemical behaviors. Since the py-GC/MS unit was unable to condense the pyrolysis vapors into a tangible amount of bio-oil, it was impossible to investigate the physical characteristics of the bio-oil such as heating value, pH value, density and viscosity. Therefore, using a fixed-bed reactor on a larger scale is one way to produce bio-oil and analyze its properties. Various types of palm wastes have been used as raw materials in these reactor type, such as palm frond,^[4-6] date palm seeds,^[7] palm fiber,^[8-11] palm empty fruit bunch,^[12-19] palm kernel shell^[20-32] and palm kernel cake.^[33-36] These studies investigated different process parameters (pretreat biomass, pyrolysis temperature, carrier gas flow rate, biomass particle size, reaction duration, employing catalyst or co-pyrolysis). However, because of the heating mechanism, pyrolysis in a fixed-bed reactor has a low heating rate and it typical consider slow pyrolysis; thus the produced bio-oil is not suitable for usage.^[37] Increasing the heating rate is one way to solve these issues^[38] by using a fast pyrolysis process which can be achieved by fast pyrolysis reactors.

In a typical fast pyrolysis process, biomass is continuously fed into a reactor (such as an auger or a fluidized-bed reactor) which enables continuous production of bio-oil. Fast pyrolysis

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is a complicated process requiring careful parameters control for producing bio-oil with finest qualities and maximum yield.^[39] These parameters included pyrolysis temperature, biomass feed rate, biomass particle size and carrier gas flow rate. The temperature during fast pyrolysis is one of the process variables that strongly influences the result. The pyrolysis temperatures from 350 to 900°C have been used to produce bio-oil from palm wastes such as palm empty fruit bunch,^[40-46] palm kernel shell,^[47-52] palm kernel cake^[53] and ivory nut.^[54] Due to differences in the type and composition of palm wastes, it appears that selection of appropriate pyrolysis temperature affects the production bio-oil.^[37] For example, pyrolysis at 478 °C using palm kernel shell and palm empty fruit bunches yielded 30.3 wt% and 36.6 wt%,^[44] respectively. However, fast pyrolysis of palm wastes has other parameters than pyrolysis temperature which also affects the process. These parameters should be studied exceeding important parameters comprising pyrolysis temperature to produce a bio-oil for optimal yield and the desired properties. In the fast pyrolysis process of palm wastes biomass, the different palm kernel shell particle sizes from 0.425-0.85 mm to 0.85-1 mm were used.^[51] It was found that using a smaller particle size of feed affected better heat transmission, resulting in a maximum bio-oil yield of 48.7 wt%. Few researchers have studied the effect of biomass feed rate on the fast pyrolysis process utilizing palm kernel shell, resulting in a maximum bio-oil yield of approximately 57-60 wt%. Some studies have found that solid-to-solid heat transfer rate increases when the using lower biomass feed rate.^[55] However, higher biomass feed rate led to a higher bio-oil yield of 48.7 wt% because the higher biomass feed rate caused a higher generation and shorter residence time of pyrolysis vapors.^[51] Lastly, the varied carrier gas flow rate from 1 to 2 l/min reduced residence time of pyrolysis vapors and inhibited the possibility of repolymerization and cracking of vapors.^[50] They are maximizing the liquid yield of 57 wt% when using palm kernel shell.^[50] When a longer residence time is required, an empty fruit bunch is used with a variable carrier gas flow rate of up to 7 l/min. They resulted the secondary reactions occur by decomposition of the volatile vapors.^[45,46]

Previous research examined the process parameters of the fast pyrolysis process using only palm kernel shell and palm empty fruit bunches. There has been a few research on palm kernel cake, which is one of the palm wastes that must find alternative uses due to its massive production volume.^[53] Ngo

et al.^[56] studies the fast pyrolysis process parameters of palm kernel cake (pyrolysis temperature, biomass feed rate, biomass particle size and carrier gas flow rate) to produce bio-oil. They condensed bio-oil using two condensers to obtain a maximum yield of 49.5 wt%. However, the improved bio-oil yield appears to be attributable to the proper condensation unit. According to Jeong *et al.*,^[53] the influence of pyrolysis temperature between 350 and 900°C was investigated using three condensers, two impact separators, and one electrostatic precipitator. They obtained a 63 wt% bio-oil yield from palm kernel cake but only explored the effect of pyrolysis temperatures. Thus, other process parameters must be evaluated in order to maximize bio-oil yield.

This work, a bench-scale fluidized bed reactor equipped with an appropriate condensation unit was used to pyrolyze palm kernel cake. The optimal properties and maximum yield of bio-oil were obtained by varying process parameters, including pyrolysis temperature, biomass feed rate, biomass particles size, and carrier gas flow rate.

2. Materials and methods

2.1 Biomass feedstock

Palm kernel cake, a byproduct of the palm waste industry in Thailand's Khon Kaen province, was used as the biomass source. After 24 hours of drying at 105 °C in an oven, it was sieved to a particle size range of 0.2-0.5 mm. Proximate, ultimate and heating value analyses of the biomass sample were compared to the typical lignocellulosic biomass of cassava rhizome. The biomass characteristics are shown in [Table 1](#). The biomass sample used in this study contained more ash than did palm kernel cake,^[53] palm kernel shells^[48,49,57-59] or even empty fruit bunches^[40-42] from other work. It is evident that the biomass samples' composition was not in the range of others palm waste biomass or typical lignocellulosic biomass.

2.2 Fast pyrolysis experiments

Fast pyrolysis experiments were carried out using a bench-scale fluidized-bed reactor unit as shown in [Fig. 1](#). The main parts of the pyrolysis unit were a reactor, a biomass hopper, a solid-gas separation set, and a bio-oil collection system. The system consisted of a 5 cm inside diameter and 40 cm height stainless steel pipe reactor, N₂ preheater, biomass feeding set, two cyclone separators, hot filter, water-cooled condenser, electrostatic precipitator (ESP), two dry ice/acetone condensers, and a cotton wool filter. Approximately 300 g of silica sand with 0.2-0.4 mm particle size was placed inside the reactor and was used as fluidizing and heat transfer medium. The sand had a bulk density of 1,500 kg/m³ and the apparent density of 3,300 kg/m³. The hot filter was filled with 10 g of glass wool. Biomass particle size ranges of <0.2, 0.2-0.5 and 0.5-0.6 mm, biomass feed rates of 50, 100 and 150 g/h, total nitrogen flow rates of 7, 9, 11, 13 and 15 L/min and pyrolysis temperatures of 400, 450, 500, 550 and 600 °C were studied. Throughout the experiment, certain variables were fixed; the cyclone and hot filter temperature of 420 °C, the ESP power

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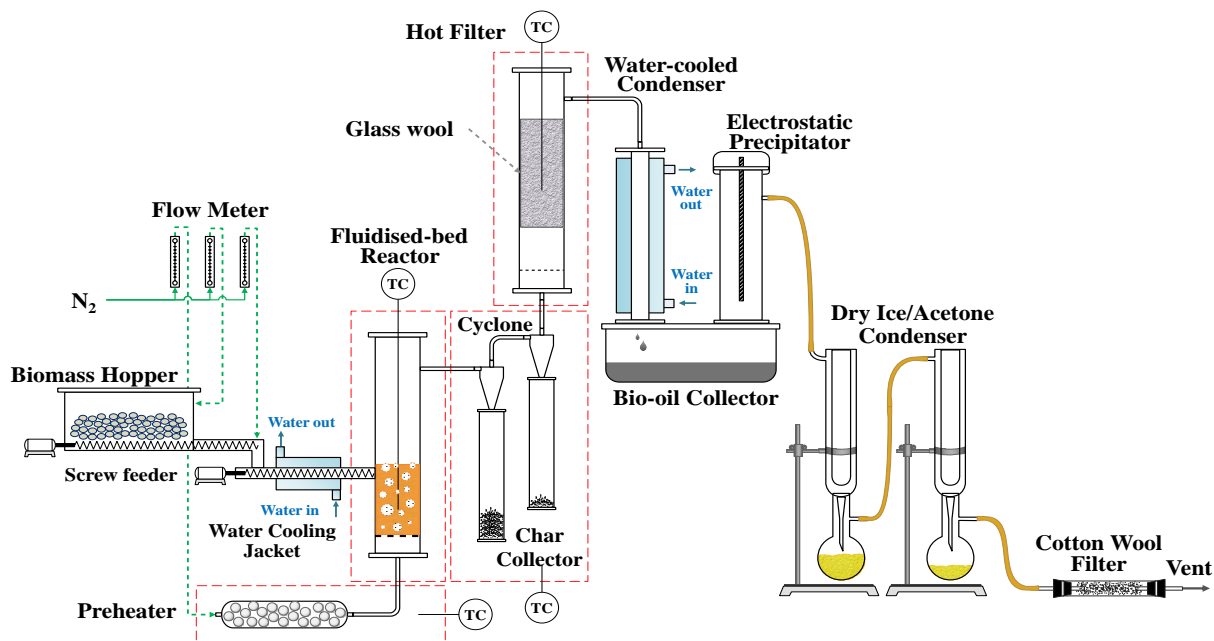


Fig. 1 Schematic diagram of the fluidized-bed unit.

Table 1. Biomass characteristics.

Analysis	Palm waste biomass			Typical lignocellulosic biomass
	This work	Palm kernel cake	Palm kernel shell	Palm empty fruit bunch Cassava rhizome
Proximate analysis (wt%)				
Moisture	7.4	-	5.9-13.6	6.4-9.6 15.3
Volatile matter	74.1	89.3	71.3-79.5	64.9-72.2 67.9
Fixed carbon (calculated by difference)	9.1	7.0	15.1-21.2	18.9-19.6 15.4
Ash	9.4	3.7	2.5-5.4	4.5-8.2 1.4
Ultimate analysis (wt%, dry ash-free basis)				
Carbon	46.0	50.8	43.6-49	41.9-44.9 45.0
Hydrogen	7.0	6.1	4.9-6.5	5.7-6.3 6.6
Nitrogen	1.4	3.1	0.3-2.9	0.7-0.9 1.1
Oxygen (calculated by difference)	45.6	39.8	45.1-51.0	37.3-49.2 47.3
Heating value (MJ/kg, dry basis)				
HHV	19.5	20.5	18.5	16.3-18.9 18.9
LHV	18.0	-	-	17.5 17.4

supply voltage of 14 kV, the water-cooling temperature of about 25 °C, the nitrogen flow rate at the biomass hopper of 1 L/min and at the screw feeder of 3 L/min.

2.3 Mass balance analysis

Liquid bio-oil, solid char and non-condensable gases are the main products from fast pyrolysis. The yields of each product were calculated by weighing all parts of the fast pyrolysis systems that mainly comprised of biomass, silica sand, fluidized-bed reactor, cyclone separators, hot filter and product collection unit, before and after each experiment. The total bio-oil yields were determined as a liquid weight from the product collection unit including water-cooled condenser, ESP, heavy bio-oil tank, dry ice/acetone condensers, light bio-oil flasks and cotton wool filter. The char yields were the

combined solid masses collected from the reactor, cyclones, hot filter and transfer line. The gas yields were calculated by difference.

Yields of organic bio-oil were calculated as non-water part of liquid product using the following equation:

$$Y_{organics} = \frac{T_{bio-oil} - \omega_{bio-oil}}{M_{dry}} \times 100$$

When:

$Y_{organics}$ = Organic bio-oil yield (wt%, dry basis)

$T_{bio-oil}$ = Total bio-oil produced (g)

$\omega_{bio-oil}$ = Total mass of water in bio-oil (g)

M_{dry} = Total dry biomass fed (g)

2.4 Bio-oil analysis

Bio-oil water content was determined by Karl-Fischer titration following ASTM E203 and using a V20 Mettler Toledo titrator.

Hydranal composite 5 was used as titrant and hydranal medium K was used as solvent.

The higher heating value (HHV) or gross heat of combustion of bio-oil on an as-produced basis was determined by a S.M.D. Torino bomb calorimeter. The testing was initiated by calibration of the bomb using approximately 1 g of benzoic acid tablet. The bomb was submerged in 2 L water. Once the fuel was recorded. The change of the temperature was used to calculate the HHV of the fuel using computer software.

The pH value of bio-oil was measured by a UB-10 Denver pH meter. The pH meter had been calibrated using standard liquids of pH 4 ± 0.02 and 7 ± 0.02 .

Bio-oil density was measured using a density bottle of 20 ml volume. The temperature was controlled at 20°C. The weight of the bio-oil at this specific volume was used to calculate the density in kg/m^3 .

Solids content of bio-oil was analyzed using a vacuum filtration technique as suggested by ASTM D7579. Ethanol was used as solvent and Whatman™ Qualitative filter papers with 2.5 μm pore size were used. The weights of the filter paper before and after filtration were used for calculation of solids content.^[60]

The kinematic viscosity of bio-oil was determined using an opaque Cannon-Fenske viscometer size 450. The temperature of the measurement was controlled using a water bath at 40°C. Prior to the experiment, standard liquids were used to obtain a factor of time and viscosity in cSt/s. Stability of bio-oil (cSt/h) was measured as viscosity change over accelerated ageing period by storing bio-oil at 80 °C for 24 hours.^[60]

Bio-oil was diluted in ethanol to 10 wt% concentration and filtered through a Filtrex nylon filter with 0.2 μm pore size before it injected. The gas chromatography/mass spectrometry (GC/MS) analysis of bio-oil was conducted using a SHIMADZU Gas Chromatograph Mass Spectrometer model GCMS-QP2010. The separation was made on a 30 m \times 0.25 mm id Restex Rtx-5MS column (Restex, USA) with 0.25 μm film thickness. The GC oven temperature was held at 60 °C for 2 min and programmed to rise from 60 °C to 270 °C at 5 °C/min. The oven was maintained at this final temperature for 5 min. The injector temperature was 270 °C with a split ratio of 100. Helium was the carrier gas with a linear velocity of 40 cm/s. The mass spectrometer was operated with electron impact (EI) mode at ion source and interface temperatures of 250 and 230 °C, respectively, with ionization energy of 70 eV. The mass range from m/z 20 to 650 was scanned with a scan event of 0.5 s. Data were collected and processed using the SHIMADZU LabSolutions GCMS solution software.

The mass yields and heating values of the pyrolysis products, along with the biomass's heating value, were used to calculate the product energy yield. The fraction of energy from biomass that was recovered in the form of pyrolysis products was calculated using the following equation:

$$\text{Energy yield (\%)} = \frac{\text{HHV}_{\text{product}} \times \text{Mass yield}}{\text{HHV}_{\text{raw material}}}$$

3. Results and discussion

The yields and properties of pyrolysis products including total bio-oil, heavy bio-oil, light bio-oil, aqueous fraction, char and non-condensable gas were measured. It is significant to note that the bio-oil collection tank at the water-cooled condenser and ESP was where the heavy bio-oil was obtained. Like typical bio-oil, it was a dark brown liquid and viscous. Other bio-oil fractions were condensed from the dry ice/acetone condenser. The light bio-oil was a dark brown liquid floating on top of the aqueous fraction. The aqueous bio-oil was a dark yellow liquid and turbid. This multilayers bio-oil occurred due to the difference of density, the presence of oxygenated compounds,^[38] higher water content and bigger organic molecules in bio-oil, which enhanced the polarity difference.^[50] Similar results have previously been observed during catalytic or non-catalytic pyrolysis of palm waste biomass.^[59] In this work, the yield of organic bio-oil as a non-water liquid product was calculated from the yields of heavy and aqueous bio-oil fractions. Small amounts of light bio-oil (<1 wt%) were found during bio-oil production.

3.1 Effect of biomass particle size on product yields

The effect of biomass particle size on product yields in experiments conducted by varied particle sizes of palm kernel cake for <0.2 to 0.5-0.6 mm. Controlled variables were pyrolysis temperature of 500°C, biomass feed rate of 100 g/h and carrier gas flow rate of 11 l/min; the result is shown in Fig. 2. The use of biomass particle size <0.2 and 0.2-0.5 mm produced total bio-oil yield of approximately 61.2-61.8 wt%. When higher biomass particle size up to 0.5-0.6 mm was used, the resulting total bio-oil yield decreased to 58.4 wt% and char yields decreased from 33.0 to 27.5 wt%. It was discovered that heat transfer was limited by larger particle sizes.^[61,62] Smaller particles affected the increase in bio-oil yield due to higher heating rate and faster reaction rate,^[39] well-pyrolyzed in biomass structure^[63] and more disintegration. Higher biomass particle size led to increased gas yields from 5.2 to 14.1 wt%.

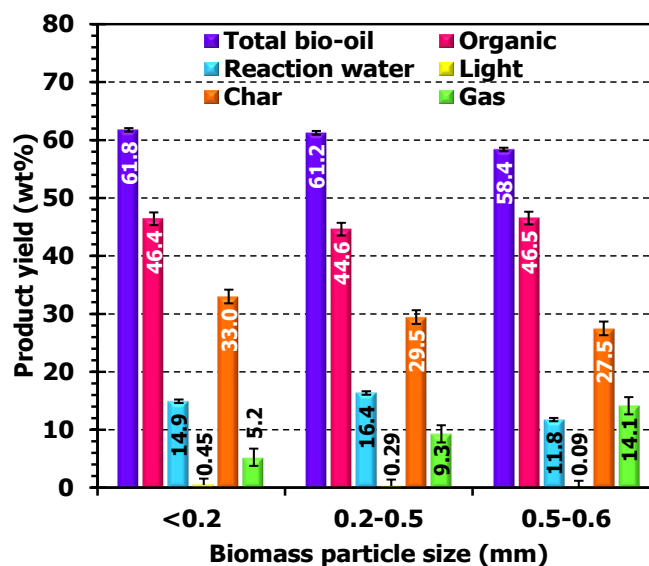


Fig. 2 Effect of biomass particle size on pyrolysis product yields.

Using a biomass particle size of <0.2 mm produced organic bio-oil yield of 46.4 wt% while biomass particle size of 0.2-0.5 mm resulted in a decreasing yield of 44.6 wt%. This could be the result of a reduced heating rate when the size of the biomass particles increases,^[63] increasing the reaction water yield from 14.9 to 16.4 wt%. However, increasing the biomass particle size to 0.5-0.6 mm resulted in higher amounts organic bio-oil and lower reaction water yield of 46.5 and 11.8, respectively. It is also possible that the cellulose to lignin ratio of the size fractions may differ,^[46] and the material's natural porosity promotes the release of volatiles without causing major morphological changes.^[63]

3.2 Effect of biomass feed rate on product yields

The effect of biomass feed rate on product yields with varied feed rate (50 to 150 g/h) using controlled variables (pyrolysis temperature 500 °C, biomass particle size of 0.2-0.5 mm and carrier gas flow rate of 11 l/min), is shown in Fig. 3. Feeding palm kernel cake at rates between 50 to 100 g/h resulted in total bio-oil yields of approximately 61.1-61.2 wt%. When a higher biomass feed rate of 150 g/h was used, the heating rate was reduced, resulting in a decrease to 57.6 wt% in total bio-oil yield. In general, the higher feed rate caused generation of more pyrolysis vapors,^[51] which led to a shorter vapor residence time preventing secondary reactions such as pyrolysis vapor cracking and polymerization.^[50,55] As result, a high feeding rate caused slow volatile release due to slow decomposition of biomass to reduced bio-oil yield.^[38]

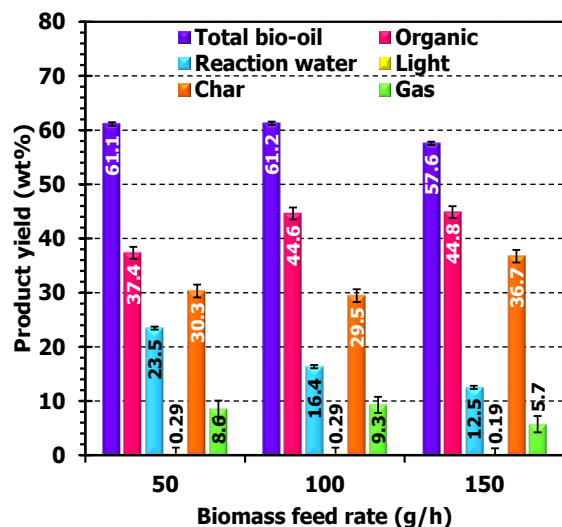


Fig. 3 Effect of biomass feed rate on pyrolysis product yields.

Organic bio-oil yield decreased from 44.6 to 37.4 wt% while lowering the biomass feed rate from 100 to 50 g/h. In this case, the secondary cracking of pyrolysis vapor into reaction water was further facilitated by the increased vapor residence time.^[50] The solid-to-solid heat transfer rate decreased when the biomass feed rate was increased from 100 to 150 g/h. Thus, organic bio-oil yield of 44.6-44.8 wt% was invariable due to the pyrolysis vapor formation not increasing.^[55] The repolymerization of pyrolysis vapor caused

by the pyrolysis vapor-char interaction results in a significantly increased feeding rate, which forms more secondary char and resulted in the highest yield of 36.7 wt%.

3.3 Effect of nitrogen flow rate on product yields

Experiments on the effect of carrier gas flow rate on product yields used total carrier gas (nitrogen) flow rates of 7 to 15 l/min (control variables were pyrolysis temperature of 500 °C, biomass particle size of 0.2-0.5 mm and biomass feed rate of 100 g/h). The results are shown in Fig. 4. Pyrolysis of palm kernel cake using nitrogen flow rate of 7 l/min resulted in total bio-oil yield of 56.1 wt%. The bio-oil yield raised to maximum yield of 61.2 wt% when using a higher nitrogen flow rate of 11 l/min. This suggests that higher flow rate decreased pyrolysis vapor residence time^[63] which caused a decrease in biochar yield from 34.9 to 29.5 wt%. Typically, a higher carrier gas flow rate through the pyrolysis zone reduces the residence time of pyrolysis vapors in the reaction area^[50] and this prevents the secondary reaction of pyrolysis vapor, forms a large quantity of char^[63] and enhances bio-oil yield.^[37] Increasing the nitrogen flow rate from 11 to 15 l/min slightly reduced the total bio-oil yield to 60.2 wt%. This could be attributed to a decrease in contact time between biomass particles and heat transfer media caused by a decrease in heat transfer coefficient at higher flow rates.^[44] A further consideration is that high gas flow rate could reduce the effective condensation of pyrolysis vapor, resulting in a lower total bio-oil yield.^[50]

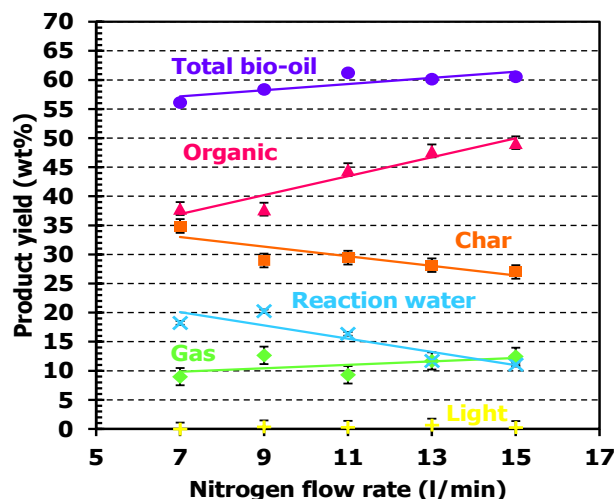


Fig. 4 Effect of nitrogen flow rate on pyrolysis product yields.

The effect of nitrogen flow rate on organic bio-oil was investigated. When the nitrogen flow rate was increased from 7 to 15 l/min, the organic bio-oil yield was significantly increased from 37.9 to 49.2 wt%. This was because of the shorter residence time due to higher flow rate causing a decrease in time spent by pyrolysis vapor in the reactor.^[37] The possibility of pyrolysis vapor decomposition was reduced.^[45,46] The increase in organic bio-oil yield was related to a decrease in reaction water yields from 18.2 to 11.1 wt%. Consequently,

it appears that less cracking promoted the production of the reaction water fraction.

3.4 Effect of pyrolysis temperature on product yields

The effect pyrolysis temperature on product yields was investigated at pyrolysis temperatures of 400 to 600 °C (control variables were pyrolysis biomass particle size of 0.2-0.5 mm and biomass feed rate of 100 g/h and carrier gas flow rate of 11 l/min). The results are shown in Fig. 5. Bio-oil production from palm kernel cake using higher pyrolysis temperature from 400 to 550 °C increased total bio-oil yields from 59.8 wt% to a maximum yield of 65.5 wt%. While using a higher pyrolysis temperature of 600 °C, the total bio-oil production was slightly reduced to 64.6 wt% due to secondary cracking of the pyrolysis vapor.^[40,54,64] Char yields were significantly decreased from 35.1 to 23.5 wt% when the pyrolysis temperature was raised. This could be attributed to the volatilization of unconverted biomass^[53] and incomplete decomposition of the biomass^[44,51] at lower temperatures.

Organic bio-oils yielded around 43.0-44.6 wt% after a fast pyrolysis procedure at temperatures ranging from 400 to 500°C. When the temperature was increased to 600 °C, the organic bio-oils increased to 47.1-49.8 wt%. This suggested that organic matter was being converted into bio-oil^[39] as a result of thermal cracking of heavy hydrocarbon compounds and secondary char decomposition,^[42,44,51] resulting in a reduced char product. In general, the bio-oil yield further decreases at higher temperatures ^[41] due to thermal decomposition that conversion of pyrolysis vapor to gas^[44] and the condensation of lignin monomers that generates highly carbonaceous char.^[37] In this case, increasing the temperature from 500 to 600 °C had no effect on the gas yields of 9.3-11.1

wt%. This was probably due to enhanced lignin degradation^[42] in the process, which may result in higher organic bio-oil production.

3.5 Bio-oil properties

The physical properties of heavy bio-oil fractions were determined and are shown in Table 2. The effect of process variables such as biomass particle size, biomass feed rate, N₂ flow rate, and pyrolysis temperature resulted in a variety of bio-oil properties. The properties of the light bio-oil fractions could not be examined due to their low concentration (less than 1 wt%). For the aqueous fractions, the properties could not be analyzed due to the more than 90 wt% of water content in the aqueous phase which is an unfavorable property for bio-oil.^[38]

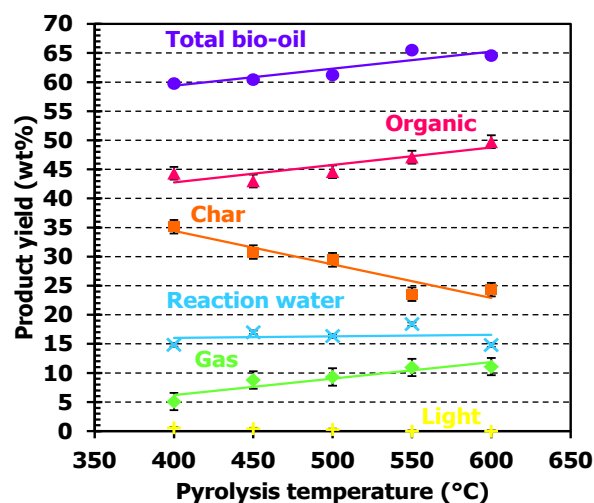


Fig. 5 Effect of pyrolysis temperature on pyrolysis product yields.

Table 2. Physical properties of heavy bio-oil fractions.

Bio-oil properties	Biomass particle size (mm)		Biomass feed rate (g/h)			N ₂ flow rate (l/min)					Pyrolysis temperature (°C)					ASTM D7544-12 Grade D	
	<212	212-500	500-500	500-100	500-150	3	5	7	9	11	40	45	50	55	600		
Water content (wt%)	6.2	7.4	5.7	7.7	7.4	8.7	7.3	8.3	7.4	7.2	6.2	4.9	5.7	7.4	7.1	6.3	≤30
HHV (MJ/kg)	27.4	28.7	25.0	29.4	28.7	26.5	25.2	27.9	28.7	28.3	25.2	28.5	27.4	28.7	29.8	29.3	≥15
pH value	3.8	4.8	3.5	4.3	4.8	4.3	4.1	4.5	4.8	4.5	4.2	4.0	4.0	4.8	4.4	4.4	Report
Density (kg/dm ³)	0.98	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	1.1-1.3
Solid content (wt%)	0.6	0.9	0.9	0.4	0.9	0.8	0.2	0.1	0.9	0.1	0.3	0.2	0.3	0.9	0.5	0.3	≤0.25
Viscosity (cSt)	141.1	16	167	18	16	192	23	20	16	21	245	18	19	16	19	175	≤125
Stability (cSt/h)	0.02	3.0	0.9	0.0	3.0	0.2	8.4	1.9	3.0	4.1	0.7	2.5	7.1	3.0	4.6	0.2	Report
		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
		2	2	2	2	2	1	2	2	1	2	2	2	2	2	2	

The water content of heavy bio-oil produced by varying the process parameters ranged around 6.2-8.7 wt%, which is lower than the water content of conventional bio-oil, which is 30 wt%.^[60] Heavy bio-oil produced by using lower pyrolysis temperatures of 400-450°C resulted in slightly decreased water content to 4.9-5.7 wt%, possibly due to the dehydration and condensation reactions of organic molecules.^[50] Water content in bio-oil is usually derived from the moisture of biomass feedstock and the several activities that occur during the fast pyrolysis process, such as dehydration, condensation, and secondary reactions.^[38,48] The amount of water in bio-oil can affect its application. Higher water content increases the fluidity and flowability of less viscous oil^[37,65] and reduces NO_x emissions.^[63] However, the excessive water content leads to a lower heating value,^[65] division into two distinct layers,^[37,50] increased ignition delay and decreased combustion rate.^[37,66]

In general, bio-oil with a larger water content has a lower heating value.^[4,37,64] For bio-oil being used as a fuel, this is a major concern. Due to its lower water content, the heating value of heavy bio-oil derived from palm kernel cake was higher than that of conventional bio-oil (16-19 MJ/kg).^[66] This suggests that the heavy bio-oil heating value of around 27.8 MJ/kg satisfied the ASTM standards for pyrolysis liquid biofuels and it was suitable for use as a fuel oil^[53] in industrial burners that can handle pyrolysis liquid biofuels or as an alternative fuel in cofiring power plants,^[67] but not in domestic heaters, small-scale boilers, engines, or maritime applications. The pH of the produced bio-oil was 3.5-4.8, which was similar to the pH value of typical bio-oil.^[68] The low pH of bio-oil, which could be attributed to carboxylic acid in the bio-oil, causes equipment problems and makes it extremely undesirable.^[38] Organic acids in bio-oil, for instance, are

particularly damaging to conventional building materials,^[63] such as aluminum, nickel, and steel-based metals.^[37]

The density of heavy bio-oil derived from palm kernel cake ranged from 0.94-0.99 kg/dm³. This value is less than the ASTM standard of 1.1-1.3 kg/dm³^[60] but higher than heavy fuel oil of 0.8 kg/dm³.^[55]

The solid content of heavy bio-oil was 0.1-0.9 wt%, which was lower than the 0.2-1 wt% of typical bio-oil.^[66] Bio-oils typically include small amounts of solid, which might lead to problems. The presence of solids in bio-oil makes it difficult to use and store. For instance, the solids in bio-oil might block injectors and erode turbine blades^[63] or they could limit the ability to store bio-oil by promoting the aging rate.^[37] The use of a higher carrier gas flow rate, as well as the particle size of the biomass being too small to be captured by the cyclone unit, may result in a high solid content in bio-oil. These issues can be solved by adjusting the process parameters or by combining the hot filter unit with a granular filter.^[69]

The chemical composition of the heavy bio-oil was identified by GC/MS analysis, as shown in Fig. 6. It contains a total of 23.8% hydrocarbon compounds, comprising 14.8% aliphatic hydrocarbons, 5.9% aromatic hydrocarbons, and 3.1% other hydrocarbons. Hydrocarbon compounds in bio-oil have a beneficial effect on HHV improvement and make the oil suitable for value-added chemicals.^[38] These suggested that the heavy bio-oil might be used in crude oil refinery units or blended with transportation fuels.^[70] Oxygenated compounds represent 76.2% of the heavy bio-oil, which includes furan, ester and saturated fatty acids such as dodecanoic, myristic, oleic, octanoic, and stearic acid. These acid compounds were generated by the decomposition of remaining palm oil constituents,^[53] which is undesirable for use and storage because it increases the opportunity of equipment corrosion.^[65]

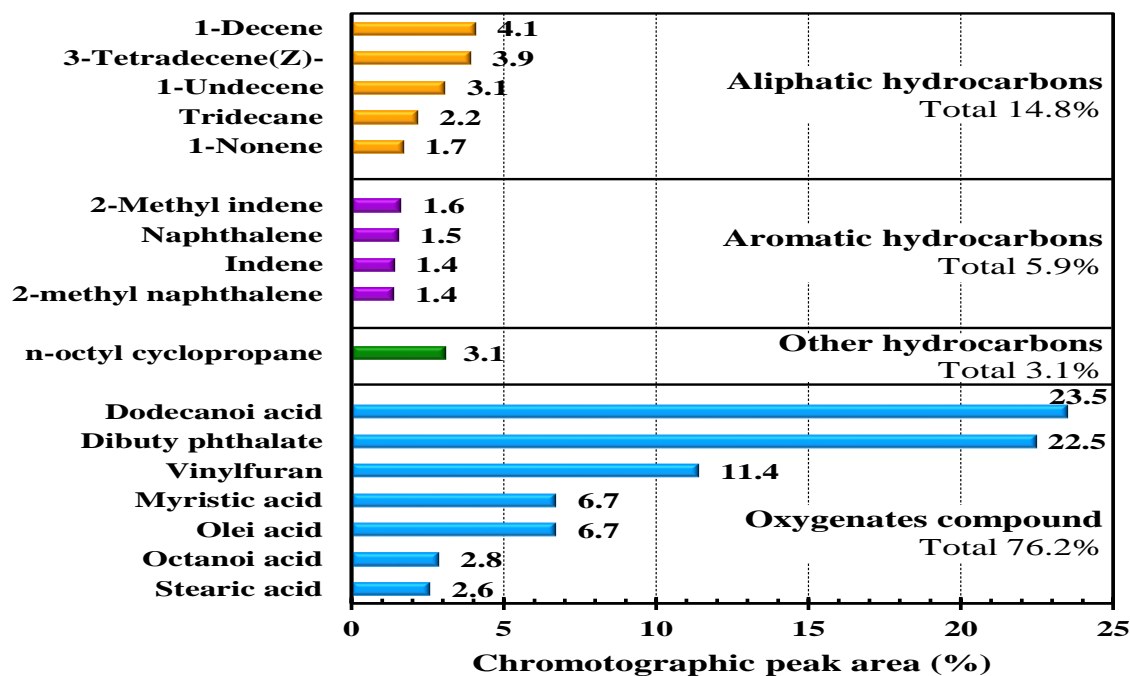


Fig. 6 Chemical composition of the heavy bio-oil based on GC/MS peak area percentage.

Due to the low water content in bio-oil, the viscosity of the produced heavy bio-oil was around 200 cSt, which exceeded ASTM criteria. Higher organic fractions were generated as a result of the bio-oil's rapid evolution of volatiles and elimination of water content.^[38] This indicated that the fast pyrolysis process from palm kernel cake employing a fluidized-bed reactor had a high heating efficiency, resulting in high viscosity bio-oil. However, it is reasonable to assume that the presence of oxygen-containing heavy organic molecules^[55,63] and lignin-derived oligomers that have recondensed after pyrolysis^[37] contributed to the high viscosity. After the aging process, heavy bio-oil has a higher viscosity, resulting in bio-oil stability of 0.02 cSt/h. Intermolecular interactions have been proposed to exist in bio-oil and these delay combustion and cause phase separation when stored.^[37,63] To avoid these constraints, bio-oils must be improved in several various ways, including upgrading during or after pyrolysis.^[71,72]

3.6 Product energy yield

Pyrolysis products derived from the process (with particle sizes of 0.2-0.5 mm, biomass feed rate of 100 g/h, carrier gas flow rate of 11 l/min and pyrolysis temperature of 550°C) were used to analyze the energy yields. The energy yields were determined by combining the mass yields and HHV of pyrolysis products from palm waste biomass, as shown in Table 3. The energy yield of bio-oil derived from palm kernel cake was 74.3%, which was greater than the range of 48.6-64.7% for palm empty fruit bunch. This suggests that the higher mass yield has an effect on energy yield because HHV of palm kernel cake (29.8 MJ/kg) was similar to palm empty fruit bunch^[44,45,52] in range of 24.9-36.1 MJ/kg. When the energy yield of palm kernel cake was compared to that of date palm waste and cassava rhizome, the bio-oil yield and HHV had significant impacts on the energy yield. Even though HHV and mass yield were in the same range in the case of palm kernel shell, a higher energy yield of palm kernel cake bio-oil was obtained. This could be attributed to variations in biomass

composition and pyrolysis process factors. Furthermore, few studies have reported improved techniques for producing bio-oil from palm empty fruit bunch by treating palm empty fruit bunches with acid and water^[40,41,73] to change its composition before using it to produce bio-oil. The results show that bio-oil yields and HHVs have increased significantly, enhancing energy yields to 44.6-84.9%.

The HHV of char produced by fast pyrolysis of palm kernel cake was 19.2 MJ/kg, which was higher than the HHV of cassava rhizome produced in the same procedure (11.3 MJ/kg). Char from palm kernel cake had a 24.0% energy yield and can be utilized as an alternative fuel as a byproduct of the fast pyrolysis process. The char produced can be co-combusted in boilers to produce electricity.^[57] Moreover, product char can be used to improve soil as well as in other carbon-based applications rather than fuel.^[39,78]

Table 3 also compares the production of bio-oil from palm kernel cake with other biomass sources including cassava rhizome, sawdust, eucalyptus wood and eucalyptus bark to assess the versatility and efficiency of the proposed pyrolysis process. The results show that although the mass yield of the palm kernel cake bio-oil was within the range of the yields of bio-oil from other biomass types (26-69 wt%). However, when considering the energy yield, it has been shown that the palm kernel cake gave the highest energy yield of 74.3% compared to others (36-51%). This suggested that the current study can potentially enhance the efficiency, sustainability, and practicality of the fast pyrolysis process for bio-oil production from palm kernel cake.

3.7 Perspectives on economic and scale-up of bio-oil production

Biomass pyrolysis offers a promising avenue for sustainable bio-oil production, yet the scarcity of viable bio-oil plants stems from the complexities of operations and lower profitability. Understanding the interplay between technological parameters and economic viability becomes imperative. The technical and economic aspects of bio-oil

Table 3. Product energy yield.

Group	Biomass		Bio-oil product			References
	Type	HHV (MJ/kg)	Yield (wt%)	HHV (MJ/kg)	Energy yield (%)	
Palm residues	Palm kernel cake	18.9	47.1	29.8	74.3	This work
	Palm empty fruit bunch	18.7-19.4	34.7-38.0	24.9-36.1	48.6-64.7	[44, 45, 52, 73]
	Washed palm empty fruit bunch	17.0-19.4	48.4-69.0	15.6-25.3	44.6-84.9	[40, 41, 52, 73]
	Palm kernel shell	15.5-18.5	23.1-48.7	17.9-30.9	28.9-61.4	[44, 51, 59, 67]
	Date palm waste	17.5	38.8	20.9	46.2	[74]
Other types of biomass	Cassava rhizome	17.4	26.2	24.1	36.2	This work
	Sawdust	19.2	69.0	10.0	35.9	[75]
	Eucalyptus wood	18.5	45.2	19.7	48.1	[76]
	Eucalyptus bark	15.7	65.0	12.2	50.5	[77]

production via fast pyrolysis from diverse biomass sources are related to key factors such as production cost, capacity, and biomass type. The cost of bio-oil production serves as a critical metric for assessing market compatibility with other biofuels. Various pretreatments, upgrades, and recycling processes significantly influence production costs. Leveraging energy integration strategies presents a viable route for biomass pyrolysis to yield bio-oil. Previously, Patel *et al.*^[79] investigated the bio-oil production cost from fast pyrolysis of 2,000 tons of woodchips per day, reporting \$1.09 per liter and suggesting an optimal plant capacity of 3,000 tons per day. Li *et al.*^[80] conducted a cost analysis of biomass in in-situ and ex-situ catalytic pyrolysis, revealing fuel-selling prices of \$1.11 per liter and \$1.13 per liter, respectively. Heat integration in pyrolysis not only ensures process sustainability through energy recovery but also reduces overall utility costs. Leveraging combustible gases generated as a co-product during fast pyrolysis can further contribute to process heat, thereby reducing operational costs and positively impacting bio-oil production costs. Economic analyses highlight the cost-reducing potential of blended feedstock and less expensive catalysts.

Moreover, higher-capacity pyrolysis plants tend to produce bio-oil more cost-effectively than smaller ones. Therefore, scaling-up to an optimal plant size is another key factor for successful commercialization. Santos *et al.*^[81] recently performed an extensive analysis of bio-oil aimed at evaluating its applicability for scale-up assessment across various reactor designs. Their investigation revealed that in the context of conventional pyrolysis processes, the impact of reactor scale variation on product composition remains limited, typically below 20%. Notably, under consistent operating conditions, the products obtained exhibit comparable compositions irrespective of reactor configuration. As such, the challenges inherent in scaling up the system can be mitigated, as altering the scale of the pyrolysis process—regardless of the reactor employed—tends to yield similar product compositions. Therefore, future efforts should focus on developing downstream methods such as solvent addition, emulsification, and electrochemical processes to upgrade bio-oil for enhanced cost-effectiveness.^[82]

4. Conclusions

The fast pyrolysis of palm kernel cake presents an efficient method for bio-oil production with a range of product yields and properties influenced by various process parameters. The experimental results highlight the significant impact of biomass particle size, biomass feed rate, nitrogen flow rate, and pyrolysis temperature on the yields and properties of pyrolysis products. The study found that smaller biomass particle sizes (<0.2 mm) resulted in higher total bio-oil yields, attributed to increased heating rates and faster reaction rates. Conversely, larger particle sizes (>0.5-0.6 mm) led to decreased bio-oil yields due to limited heat transfer. Biomass feed rate also played a crucial role, with higher feed rates

resulting in decreased bio-oil yields due to shorter vapor residence times and increased secondary reactions. Moreover, nitrogen flow rate affected bio-oil yields, with higher flow rates enhancing bio-oil production by reducing pyrolysis vapor residence times. Pyrolysis temperature significantly influenced bio-oil yields, with higher temperatures generally increasing bio-oil production due to enhanced thermal cracking of heavy hydrocarbon compounds. However, excessively high temperatures led to secondary cracking of pyrolysis vapor, resulting in reduced bio-oil yields. The physical properties of the produced bio-oil, including water content, pH, density, solid content, viscosity, and stability, varied depending on the process parameters. Notably, bio-oil derived from palm kernel cake exhibited favorable properties for use as a fuel oil replacement in industrial burners or co-firing power plants, meeting ASTM standards for pyrolysis liquid biofuels. Analysis of the energy yields demonstrated the potential of palm kernel cake as a feedstock for bio-oil production, with high energy yields comparable to other biomass sources. Additionally, the char produced as a byproduct of the pyrolysis process showed potential applications as an alternative fuel or soil amendment. Overall, this study provides valuable insights into optimizing the fast pyrolysis process of palm kernel cake for bio-oil production, contributing to the development of sustainable bioenergy solutions. Further research could focus on refining process parameters including upgrading to enhance bio-oil quality and exploring novel applications for bio-oil and char byproducts.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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