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Characterization of products from slow pyrolysis of palm kernel cake and cassava pulp residue

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Abstract−Slow pyrolysis studies of palm kernel cake (PKC) and cassava pulp residue (CPR) were conducted in a fixed-bed reactor. Maximum liquid yield (54.3 wt%) was obtained from PKC pyrolysis at 700 °C, heating rate of 20 °C/min, N_2 gas flow rate of 200 cm^3/min and particle size of 2.03 mm. Fuel properties of bi-oils were in following ranges: density, 1.01-1.16 g/cm^3; pH, 2.8-5.6; flash point, 74-110 °C and heating value, 15 MJ/kg for CPR oil and 40 MJ/kg for PKC oil. PKC oil gave main contents of n-C_8-C_{18} carboxylic acids, phenols, and esters, whereas CPR oil gave the highest amount of methanol soluble fraction consisting of polar and non-volatile compounds. On gas compositions, CPR pyrolysis gave the highest yield of syngas produced, while PKC pyrolysis offered the highest content of CO_2. Pyrolysis chars possessed high calorific values in range from 29-35 MJ/kg with PKC char showing a characteristic of reasonably high porosity material.

Key words: Biomass, Pyrolysis, Bio-oil, Fuel Properties, Chemical Compositions

INTRODUCTION

The increase in energy demand but with unstable supply and high price of fossil fuels requires increasing development and utilization of renewable energy. Biomass, which constitutes the largest portion of renewable energy sources, has shown great promise in solving the energy crisis due to its abundant supply, being less dependent on political factors and neutral emission of CO_2. A number of processes to produce energy from biomass are available through thermal conversion processes of combustion, gasification and pyrolysis. Of these processes, biomass pyrolysis, a thermochemical decomposition of organic materials at elevated temperatures in the absence of oxygen, is a viable route for efficient and economical production of clean alternative energy in forms of solid (char), liquid (tar and an aqueous solution of organic materials) and gases. Apart from being a source of fuel, the liquid oil can also be used as a starting feedstock for the recovery of many valuable chemical species [1].

The pyrolysis liquid product or bio-oil contains chemicals with many different functional groups such as acids, sugars, alcohols, ketones, aldehydes, phenols and their derivatives, furans and other mixed oxygenates [2]. Bio-oil derived from the pyrolysis process possesses low pH value between 2 and 3.7 and has higher density of about 1,200 kg/m^3, higher viscosity (25 cP up to 1,000 cP) and lower heating value (14-18 MJ/kg) compared to those of transport fuel oil [3,4]. For the pyrolysis gases, they have low to medium heating values that can be burned for power generation or used as a heating medium for drying processes [5]. Char produced from biomass pyrolysis contains low ash content and has high heating value (HHV) of 23-32 GJ/tonne [6].

Distribution of pyrolysis products depends on such operating conditions as type of feedstock, reaction time, pyrolysis temperature and sweep gas flow rate [7,8]. To obtain high liquid yield, the pyrolysis conditions require high heating rate, moderate temperature (450-550 °C) and short vapor product residence time [9]. Higher proportion of gas product is obtained from applying high temperature, low heating rate and long residence time, while slow heating at lower temperatures and long vapor residence time favor the formation of char product [9-11]. Also, cellulosic composition of biomass and process variables including pyrolysis temperature and heating rate can have a profound influence on the chemical compositions of both gas and liquid products [5,12,13].

The biomass feedstocks used for pyrolysis study in the present work were chosen from local availability of potential agricultural wastes which are cassava pulp residue and oil-palm kernel cake. Cassava pulp residue is discarded from tapioca flour mills, and palm kernel cake is a solid waste abandoned from palm-oil milling processes. Presently, about 17 million tons of cassava are produced annually in Thailand from which about 1.7 million tons of cassava pulp residue are generated each year [14,15]. Almost all of cassava pulp residue is utilized as a low-price carbohydrate source for veterinary food [16]. Considering the total amount of this solid waste being produced each year, it is tempting to use this low cost raw material for producing a variety of valuable products, for example, a chemical feedstock or fuels in different forms through the application of pyrolysis process. Although the annual output of palm kernel cake is much lower than cassava pulp residue of only 0.06 million tons per year [17], it is considered to have a potential for use as a precursor in the pyrolysis process. This stems from the fact that palm kernel cake is a residue left after oil extraction so that it is expected to produce bio-oil with reasonably high heat content.

This work focuses on studying the effect of biomass type and pyrolysis conditions (temperature, particle size, N_2 sweeping gas flow rate and heating rate) on product yields of solid char, pyroly-

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sis liquids and gases. A fixed bed reactor is employed in this work due to its simple construction and relatively low operating cost. The derived pyrolysis products were also characterized for their chemical and fuel properties to assess their potential uses as a source of renewable fuel and/or chemical feedstock.

EXPERIMENTAL

1. Feedstock Preparation and Characterization

Biomass feedstocks (cassava pulp residue and palm kernel cake) were milled and sieved to obtain an average particle size of 0.11 mm for biomass characterization and average particle sizes of 0.71, 1.35, 2.03, 3.56 mm for pyrolysis experiments. The sieved biomasses were dried at 120 °C for 24 hours in an oven to speed up the removal of excess moisture and then left at room condition until no weight change was noticed. The drying was carried out in order to study the pyrolysis products produced solely from thermal decomposition of the biomass feed without the occurrence of secondary products from reactions involving the excess moisture, for example, water-gas reaction or steam reforming and to prevent the possible increase of water content in the bio-oil product from vapor condensation. The dried biomass samples were characterized for bulk density, true density (Helium pycnometer, AccuPyc 1330 Micromeritics), proximate analysis (moisture content (ASTM D2867-95), volatile content (ASTM D5832-95), ash content (ASTM D2866-94) and fixed carbon content (by difference)), elemental analysis (CHNS/O analyzer, Perkin Elmer PE2400 series II) and heating values (ASTM D3286-96). In addition, thermal decomposition behavior of biomass raw materials was determined using a thermogravimetric analyzer (SDT 2960 simultaneous DSC-TGA model, TA instruments). For this analysis, a sample of 10-15 mg was heated from room temperature to 850 °C with the heating rate of 20 °C/min under a nitrogen flow of 100 cm^3/min. The fractional weight remaining as a function of increasing temperature was recorded continuously.

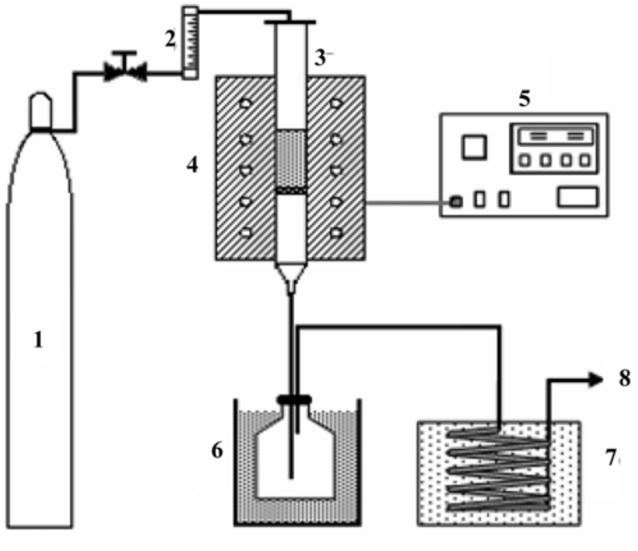


Fig. 1. Schematic diagram of the fixed-bed pyrolysis apparatus.

1. N_2 tank
2. Gas flow meter
3. Fixed bed reactor
4. Vertical tube furnace
5. Furnace controller
6. Condenser 1 (mixture of salt-ice)
7. Condenser 2 (mixture of glycerin-water)
8. Non-condensable gases to exhaust

2. Pyrolysis Experiments

The pyrolysis of biomass samples was performed in a stainless steel fixed-bed reactor (4.5 cm i.d. and 46 cm long) inserted in a vertical tube furnace (PTF 12/50/450, Protherm Electrical Furnaces). Fig. 1 shows the schematic diagram of the experimental set up used in this work. About 100 g of palm kernel cake or 50 g of cassava pulp residue was loaded into the reactor. The biomass sample was then heated from room temperature to the final desired pyrolysis temperature (300-800 °C) at the specified heating rate (5-20 °C/min) and held at this temperature for the required period of time. During the pyrolysis run, ultra high purity grade of nitrogen gas (99.9995% of N_2 supplied by TIG, Thailand) was continuously supplied in the downward direction through a fixed bed of biomass particles at a constant selected flow rate (50-600 cm^3/min). Nitrogen gas of high purity was used to avoid the concomitant reactions that may occur by the contaminant gases such as O_2, H_2O and CO_2. The pyrolysis vapor produced flowed through two condensers connected in series in which the entrained char and liquid product were collected. The first condenser utilized a salt-ice mixture in a bath maintaining at −6 to −8 °C. The second condenser operated at −20 °C using a temperature-controlled water bath filled with a glycerin-water mixture. The pyrolysis was run until no liquid was collected (by visual observation) and no major gases (excluding N_2) were produced as checked by GC analysis, usually taking about 60 min after the final pyrolysis temperature was attained. During the course of experimental runs, non-condensable gas was periodically sampled for its gas composition analysis. The char products left in the reactor and in the liquid oil from the two condensers (recovered by paper filtration) were collected and weighed and the corresponding product yields were calculated based on the mass of initial biomass feed. Gas yield was calculated by mass balance, knowing the yields of total collected solid char and liquid oil.

3. Analysis of Pyrolysis Products

3-1. Liquid Product

Bio-oils collected from the pyrolysis process were analyzed for their physicochemical properties. It was noted that the bio-oil obtained from palm kernel cake consisted of two immiscible layers of oil and aqueous phase, with the latter being separated by decanting. However, bio-oil derived from pyrolysis of cassava pulp residue gave a homogeneous single liquid phase. Water remaining in this derived crude oil was later removed and its quantity determined by refluxing the oil with toluene solution using the Dean-Stark method (ASTM D95-83).

The chemical compositions of dewatered bio-oils derived from the two biomasses at two different pyrolysis temperatures of 500 and 700 °C were analyzed by a gas chromatograph. However, due to the presence of a large number of chemicals in bio-oil, it was necessary to fractionate the oil sample into different fractions prior to the chemical analysis. Dewatered bio-oil was first fractionated by employing the technique of liquid chromatography as follows. Silica gel of 70-230 mesh (63-300 μm) size fraction was packed in a glass column of 2 cm inside diameter and 10 cm high. Next, 0.25 g of dewatered bio-oil sample was poured into the column and then eluted successively with pentane (10-20 cm^3), toluene (20-30 cm^3), diethyl ether (30-40 cm^3) and methanol (80 cm^3) to obtain aliphatic, aromatic, oxygenated and polar fractions, respectively. The fractions extracted with pentane, toluene and diethyl ether were further analyzed by gas chromatography/mass spectrometry (GC/MS). The amount of each solvent used (except methanol) was determined by trial and error based on the criterion that the solvent quantity used should be low enough to extract all affinitive chemicals and yet giving sufficiently high concentration of eluted species for accurate interpretation of GC/MS results. Methanol was the last solvent used to extract all remaining components, including non-volatile compounds and the heaviest hydrocarbon fraction of asphaltenes. A relatively high quantity of methanol was employed to ensure a complete leaching out of chemical species, as traced by the change in the color of column effluent from dark to a clear liquid solvent. The collected methanol fraction could not be directly analyzed and quantified by GC/MS, and thus it was dried in a rotary evaporator to evaporate out the solvent and the thick liquid residue weighed.

The GC/MS system used is Varian Cp-3800 gas chromatograph with a mass selective detector and the column used is VF-5MS capillary column (30 m×0.39 mm, 0.25 μm film thickness). The flow rate of helium carrier gas was 0.5 cm^3/min and injector temperature of 260 °C. The temperature program used was as follows:

40 °C for 6 min followed by heating to 270 °C at 5 °C/min
270 °C for 8 min followed by heating to 300 °C at 15 °C/min
300 °C for 10 min followed by heating to 320 °C at 20 °C/min
30 min dwell time at 320 °C

The types and concentrations of chemical constituents in the oil fractions were obtained from the spectra library of NIST MS Search 2.0 and the known concentrations of standard chemicals.

In addition, the crude bio-oil and water-free bio-oil obtained under the conditions giving maximum liquid yields were also measured for their basic fuel properties, including boiling range distribution (ASTM D86-96), calorific value (ASTM D240-92), flash point (ASTM D93-97), pour point (ASTM D97-96a), density (Gay-Lussac bottle), viscosity (ASTM D445-96), carbon residue (ASTM D524-97) and ash content (ASTM D482-95).

3-2. Char Product

Chars derived from pyrolysis of the two biomasses and at two pyrolysis temperatures (500 and 700 °C) were characterized for bulk density, true density (He pycnometer, Accupyc 1330 Micromeritics), proximate analysis (moisture content (ASTM D2867-95), volatile content (ASTM D5832-95), ash content (ASTM D2866-94) and fixed carbon content (by mass balance)), elemental analysis (CHNS/O analyzer, Perkin Elmer PE2400 series II), heating value (ASTM D3286-96) and porous properties (surface area analyzer, Micromeritics ASAP 2010).

3-3. Gas Product

Gas products were identified and quantified by a gas chromatograph (GC-14B, Shimadzu) with a thermal conductivity detector (TCD). Porapak Q column (1 m long and 4 mm i.d.) was used for CO_2 analysis, whereas molecular sieves 5A column (1 m long and 4 mm i.d.) was used for the analysis of H_2, O_2, N_2, CO and CH_4. Operational conditions for GC were argon carrier gas flow rate of 25 cm^3/min, injector temperature of 80 °C, column temperature of 100 °C for molecular sieves 5A column and 50 °C for Porapak Q column, and detector temperature of 100 °C.

Table 1. Biomass properties and chemical compositions

Properties	Biomass	
	Palm kernel cake	Cassava pulp residue
Bulk density (g/cm^3)		
Particle size of 0.71 mm	0.600	0.348
Particle size of 1.35 mm	0.573	0.326
Particle size of 2.03 mm	0.568	0.294
Particle size of 3.56 mm	0.501	0.284
True density (g/cm^3)	1.385	1.507
Proximate analysis (Dry basis) (wt%)		
Volatiles	79.57	81.98
Fixed carbon	16.74	11.83
Ash	3.69	6.19
Elemental analysis (wt%)		
C	47.19	35.89
H	6.38	5.47
O	43.28	58.27
N	3.15	0.36
H/C (mole ratio)	1.62	1.83
O/C (mole ratio)	0.69	1.22
Gross heating value (MJ/kg)	21.91	22.41

RESULTS AND DISCUSSION

1. Feedstock Characterization

Table 1 shows the basic physical properties and compositions of the two biomasses studied. The average particle size of the biomass feed in the range 0.71-3.56 mm exerts a slight effect on the bulk density with smaller size particles giving higher bulk density. Bulk density of palm kernel cake is about twice that of cassava pulp residue but the true densities of both biomasses are not greatly different: 1.385 g/cm^3 and 1.507 g/cm^3 for palm kernel cake and cassava pulp residue, respectively. This indicates that particles of palm kernel

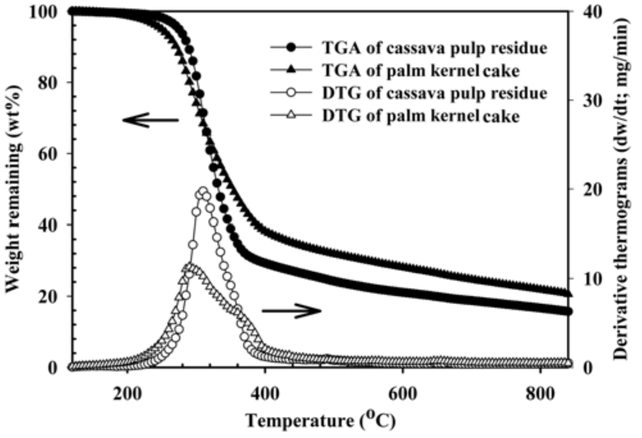
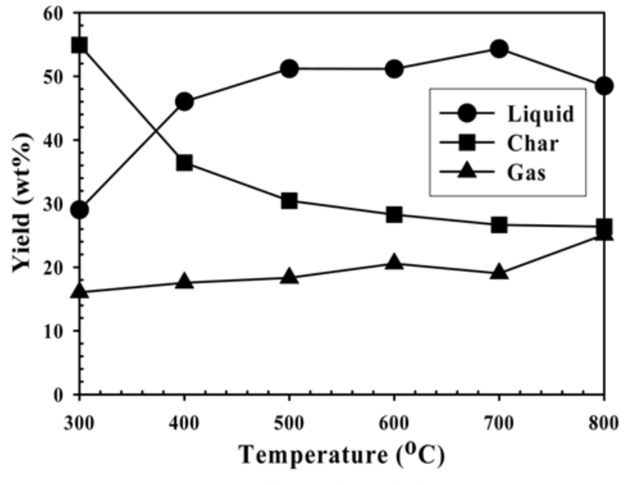


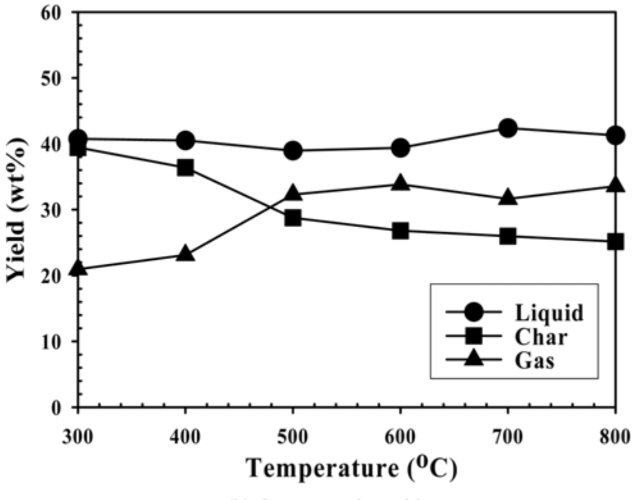
Fig. 2. Thermal analysis (TGA and DTG) of cassava pulp residue and palm kernel cake used in the pyrolysis study (average particle size of 0.11 mm, heating rate of 20 °C/min and nitrogen flow rate of 100 cm^3/min).

cake are more densely packed than those of cassava pulp residue. Proximate and ultimate analyses show that the main composition of biomasses is volatile content with carbon and oxygen being the major elements. The two biomasses gave approximately the same heating value of about 22 MJ/kg.

Fig. 2 shows the thermal analyses of the oil-palm kernel cake and cassava pulp residue, presented as weight percent remaining (TGA curves) and its first derivative (DTG curves). The plots indicate that the main pyrolysis decomposition of both raw materials occurred in the range 250-400 °C. Obviously, the thermal decomposition of these biomasses will result from the decomposition of their lignocellulosic components (hemicellulose, cellulose and lignin), which generally decompose over the temperature range of 200-400 °C [18]. Lignin usually decomposes first at the lowest temperature and continues up to the temperature around 900 °C. Hemicellulose and cellulose decompose over the temperature range of 160-360 °C and 240-390 °C, respectively [19]. It can be also observed that there was only one distinct peak of DTG curve for cassava pulp residue, while the palm kernel cake showed one major peak with a small shoulder at 350 °C. The maximum decomposition rate of palm kernel cake and cassava pulp residue occurred at 290 and 310 °C, respectively.



(a) Palm kernel cake



(b) Cassava pulp residue

Fig. 3. Effect of pyrolysis temperature on product yields (pyrolysis conditions: particle size of 2.03 mm, N_2 flow rate of 200 cm^3/min and heating rate of 20 °C/min).

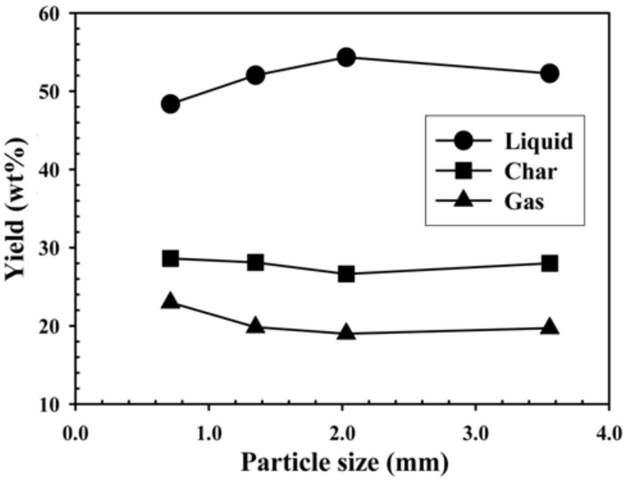
2. Effect of Pyrolysis Conditions on Product Yields

2-1. Pyrolysis Temperature

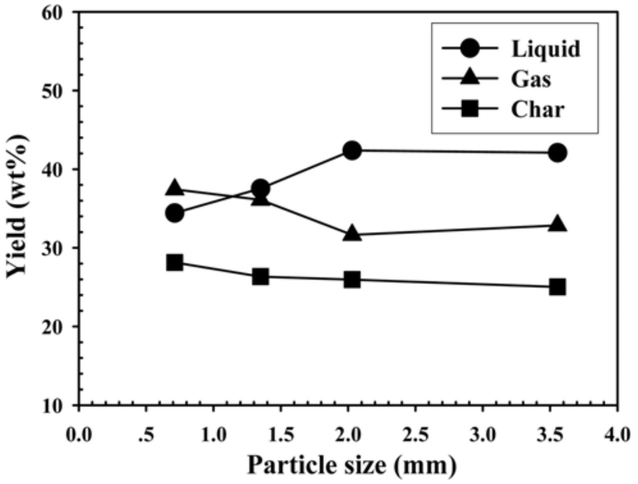
Fig. 3 shows the effect of pyrolysis temperature on the product yields of palm kernel cake and cassava pulp residue (pyrolysis conditions: average particle size 2.03 mm, N_2 flow rate 200 cm^3/min and heating rate 20 °C/min). Over the temperature range from 300-800 °C, char yields derived from pyrolysis of palm kernel cake and cassava pulp residue varied in the range of 26.4-54.9 wt% and 25.2-39.4 wt%, respectively. The char yield decreased sharply from 300 to 500 °C, followed by a slow decrease at higher temperatures and approaching a constant value at 800 °C. For palm kernel cake, the gas yield slowly rose almost linearly from 16.1 to 25.1 wt% with increasing the pyrolysis temperature from 300 to 800 °C. Higher gas yields varying from 21.0-33.8 wt% were obtained with cassava pulp residue. For this case, the increase of gas yield was more pronounced up to 500 °C and became relatively constant at higher pyrolysis temperatures. For palm kernel cake, the liquid yield obtained increased from 29.0 to 54.3 wt% with increasing temperature in the range from 300-700 °C but decreased to 48.5 wt% at 800 °C. On the other hand, increasing the temperature from 300 to 800 °C did not greatly alter the liquid yield for cassava pulp residue pyrolysis, although pyrolysis at 700 °C still gave the maximum in liquid yield. Previous studies have demonstrated that the optimum pyrolysis temperature that produces the maximum in liquid yield depends on pyrolysis conditions and reactor configuration with biomass type showing the most distinct effect [20,21]. It is further noted from Fig. 3 that at the temperature higher than 700 °C, there was a sudden increase of gas yield with a corresponding decrease of liquid yield for palm kernel cake but this effect was not so pronounced for cassava pulp residue. This increase in the gas yield could result from the increased rate of char decomposition at the high pyrolysis temperature [22,23]. At the same time, pyrolysis at this high temperature could also produce more gaseous product from decomposition of liquid product, hence giving the decreasing of liquid yield. Similar observation was also reported in the previous investigations [24, 25] that the liquid yields derived from pyrolysis of rapeseed and cotton cake tended to decrease at pyrolysis temperatures higher than 500 °C.

2-2. Particle Size

The effect of particle size in the range of 0.71-3.56 mm on product yields was studied at 700 °C with the heating rate of 20 °C/min and N_2 flow rate 200 cm^3/min. Fig. 4 shows that the pyrolysis of the two biomasses with the average size of 2.03 mm gave the maximum in liquid yield of 54.3 wt% and 42.4 wt% for palm kernel cake and cassava pulp residue, respectively. For particle sizes smaller than 2.03 mm, higher gas and char yields but a lowering in liquid yield were obtained as the particle size was decreased. It is likely that the smaller size of biomass particles could affect greater heat transfer because of less temperature gradient inside the particle, thus giving higher yields of released gases and volatiles. In addition, the denser packing of smaller size particles (see Table 1 for bulk density property) could impede the flow of sweeping gas. This would prolong the pyrolysis products to stay in the reaction zone, thus allowing secondary reactions via thermal cracking, repolymerization, and

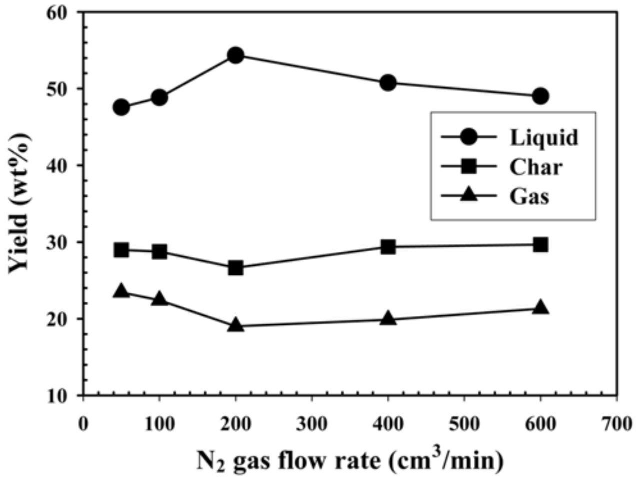


(a) Palm kernel cake

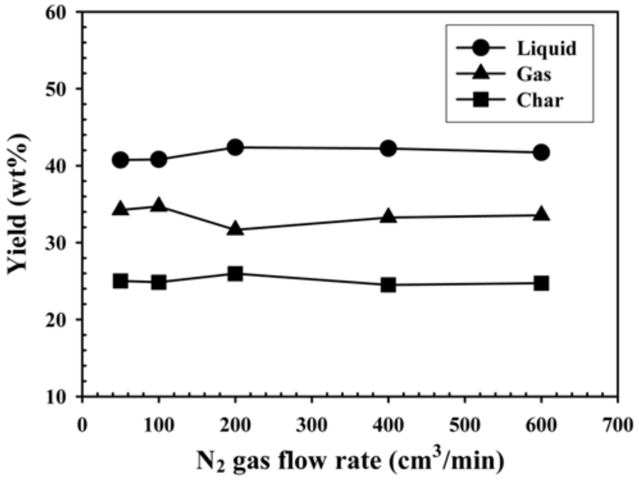


(b) Cassava pulp residue

Fig. 4. Effect of particle size on product yields (pyrolysis conditions: temperature of 700 °C, heating rate of 20 °C/min and N_2 flow rate 200 cm^3/min).



(a) Palm kernel cake



(b) Cassava pulp residue

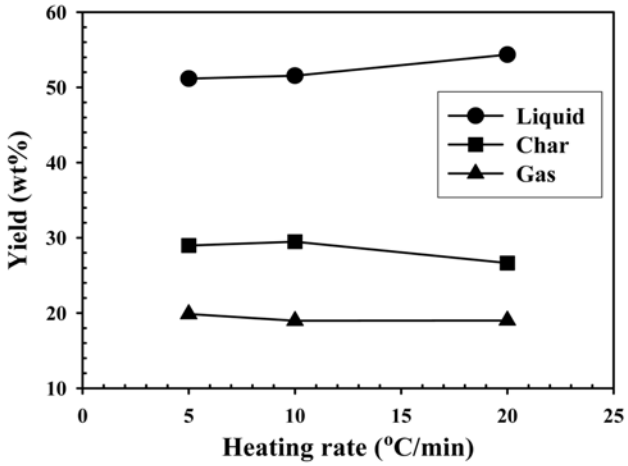
Fig. 5. Effect of N_2 gas flow rate on product yields (pyrolysis conditions: temperature of 700 °C, heating rate of 20 °C/min, and particle size of 2.03 mm).

recondensation to occur, whereby giving additional decomposition of higher molecular weight volatiles to gas product with reduction in the amount of liquid product and increased formation of solid char [24].

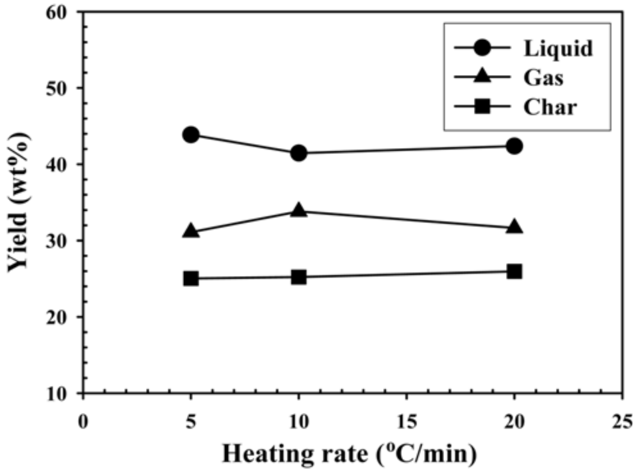
For particle sizes larger than 2.03 mm, the variation in product yields was not so sensitive to the change in particle size, with slight decreasing of liquid product and small increasing of gas and char products being observed for increasing in particle size. This effect could result from heat and mass transfer resistances in larger size particles. This would cause a temperature gradient and an increase in the diffusion path of volatile matters inside the particle, thus leading to the increased char yield and decreasing of liquid product. These effects were also observed by Guo and Lua [26], from which they found that pyrolysis of particles larger than 2 mm was controlled by heat and mass transfer resistances, resulting in slower rate of pyrolysis and lower conversion.

2-3. Sweeping Gas Rate

Pyrolysis of palm kernel cake and cassava pulp residue at different N_2 gas flow rates was studied under the following conditions: pyrolysis temperature of 700 °C, heating rate of 20 °C/min, and average particle size of 2.03 mm. Results shown in Fig. 5 indicate that the application of N_2 flow rate in the range of 50-600 cm^3/min exerted a definite influence on the product yields for kernel cake pyrolysis, whereas the effect was much less for the pyrolysis of cassava pulp residue. Maximum in liquid yields of 54.3 wt% and 42.4 wt% was obtained at N_2 flow rate of 200 cm^3/min for palm kernel cake and cassava pulp residue, respectively. At N_2 flow rates lower than 200 cm^3/min, lower N_2 flow rate gave lower liquid yields with correspondingly higher yields of gas and char. Again this may be reasoned that lower gas flow rate would lead to longer residence time for the sweeping gas, which would allow secondary reactions of pyrolysis products such as thermal cracking of higher molecular weight components to produce more gaseous products and reactions of repolymerization and condensation to form additional char and coke [24]. On the other hand, N_2 gas flow rate higher than 200 cm^3/min would provide the opposite trend for the product yield. This could be explained by the decreasing of pyrolysis temperature of biomass particles and shorter residence time for the pyrolysis



(a) Palm kernel cake



(b) Cassava pulp residue

Fig. 6. Effect of heating rate on product yields (pyrolysis conditions: temperature of 700 °C, N_2 flow rate of 200 cm^3/min and particle size of 2.03 mm).

products to stay in the reaction zone when higher N_2 gas flow rate is applied. The overall effect would lead to less decomposition of feedstock and the derived products, thus giving lower liquid yield and higher yield of char.

2-4. Heating Rate

In studying the effect of heating rate, the pyrolysis was performed under the following conditions: heating rate in the range of 5-20 °C/min, pyrolysis temperature of 700 °C, N_2 flow rate of 200 cm^3/min and particle size of 2.03 mm. The obtained results are shown in Fig. 6. It is noted that the product yields including liquid, char and gas were not greatly dependent on the applied heating rate over the relatively narrow range from 5-20 °C/min. The largest variation was only 3.2% which was observed for the liquid yield derived from pyrolysis of palm kernel cake. This result agreed with the work of Putun et al. [27] and Tsai et al. [28], which showed that pyrolysis study at temperature from 500-700 °C had no important effect of heating rate on product yields in the range of 7-40 °C/min and 100-500 °C/min, respectively. However, the work of Karaosmanoglu et al. [29] indicated that heating rate higher than 30 °C/min provided higher yields of liquid and gas products and lower char yield than those derived from pyrolysis at 10 °C/min. This observation on the effect of heating rate, however, did not significantly affect the amount of liquid product when the pyrolysis was undertaken at the higher temperature of 650 °C. Thus, based on the results from these limited investigations, it is hypothesized that heating rate should have less effect on the product yields at a relatively high pyrolysis temperature (e.g., 700 °C in this work) since the heating-up period to this high temperature for any applied heating rate must in effect pass the main devolatilization temperature range (e.g., 250-400 °C in this work) where major weight loss has already occurred.

3. Bio-oil Properties

3-1. Physical and Fuel Properties

The pyrolysis liquids derived from the two types of biomass studied differed in both color and odor. Liquid oil from the pyrolysis of cassava pulp residue showed a single transparent phase with dark

Table 2. Fuel properties of two bio-oils derived from pyrolysis conditions giving maximum bio-oil yield (pyrolysis conditions: temperature of 700 °C, heating rate of 20 °C/min, particle size of 2.03 mm and N_2 flow rate of 200 cm^3/min)

Properties	Diesel oil	Heavy fuel oil	Bio-oil			
			Palm kernel cake		Cassava pulp residue	
			Crude oil[a]	Water removed	Crude oil[b]	Water removed
Calorific value (MJ/kg)	45.0-46.0	40.0	-	40.0	*	14.9
Flash point (°C)	75	-	-	74	98	110
Pour point (°C)	-2	-	-	1	-6	-17
pH	-	-	-	5.62	2.95	2.82
Density at 30 °C (g/cm^3)	0.78[c]	0.94[c]	-	1.01	1.10	1.16
Viscosity at 40 °C (cSt (mm^2/s))	1.8-4.1	180[d]	-	58.72	1.46	28.30
Ramsbottom carbon residue (wt%)	-	-	-	5.39	2.57	4.43
Ash content (wt%)	0.01	0.1	-	0.041	0.081	0.167
Water content (wt%)	-	0.1	57.00	<0.6	56.41	-

[a] Phase separation between oil and water
[b] Homogeneous phase of oil-water
[c] density at 15 °C (g/cm^3)
[d] Viscosity (cSt (mm^2/s)) at 50 °C
*Not measurable

red-brown color. Crude oil from palm kernel cake had opaque dark color and gave the separation of oil-aqueous phase, from which the top aqueous solution could be easily separated from the oil phase by decanting. Generally, bio-oil and water can mix to form a single phase chemical solution but the phase separation can occur when the water content exceeds about 30 to 45 wt% [5]. Moreover, there was evidence that the separation of oil-aqueous phase may result from the immiscible chemicals presenting in the pyrolysis liquid [4].

Table 2 compares the fuel properties of bio-oils derived from the two biomasses for pyrolysis conditions that produced the maximum in bio-oil yield and those of No. 2 diesel oil [30] and heavy fuel oil [31]. Ranges of some important fuel properties of the derived bio-oils are as follows: density, 1.01-1.16 g/cm^3; pH, 2.8-5.6; flash point, 74-110 °C and pour point, −17-1 °C. According to these results, bio-oils possess some advantageous properties of higher flash point and lower pour point in comparison with diesel. However, it was observed that the crude bio-oils contained relatively high water contents: ~56 wt% for cassava pulp residue and ~57 wt% for palm kernel cake. Viscosity of crude oil from cassava pulp residue at 40 °C was relatively low, about 1.5 cSt. However, after water removal, viscosities of both bio-oils had increased substantially (28.3 cSt for cassava pulp residue oil and 58.7 cSt for palm kernel cake oil). In addition, removing of water from the oils caused about twice an increase in the values of ramsbottom carbon residue and ash content. It should be noted that the oil calorific value could only be determined when water was removed from the raw oils and the measured values are 14.9 and 40.0 MJ/kg for cassava pulp residue and palm kernel cake, respectively. The much lower heating value of dewatered bio-oil from cassava pulp residue is indicative of large amounts of oxygenated compounds in this oil; our results from elemental analysis indicated that oxygen contents of bio-oils from cassava pulp residue and palm kernel cake were 48.7 and 19.0 wt%, respectively. It was further noticed that the heating value of oil derived from palm kernel cake pyrolysis had the same value as that of heavy fuel oil. Distillation curves of the two bio-oils are displayed and compared with that of diesel fuel as shown in Fig. 7. Crude bio-oil from cassava pulp residue pyrolysis gave the constant boiling range distribution at about 100 °C for the first 75 vol% of the collected liquid, showing that water and/or light oxygenated compounds such as alcohols and acids are major components in the bio-oil. Both of dewatered bio-oils showed similar pattern of distillation curves to that of diesel fuel, with kernel cake derived oil giving closer boiling range distribution to that of diesel fuel. By comparing the important fuel properties between bio-oils and petroleum-based fuels, it is seen that based on its heat content, we can use bio-oil from palm kernel cake pyrolysis directly without pretreatment as a substitute for heavy fuel oil. When compared with bio-oil from commercial fast pyrolysis of wood and bagasse [32], palm kernel cake derived oil from this simple slow pyrolysis offers about twice higher in heating value (40 versus 15-20 MJ/kg oil) but a 17% less in terms of total heating value (10 versus 12 kJ/kg biomass). To use bio-oil from palm kernel cake in diesel engines, however, steps must be taken to lower the oil viscosity to an acceptable level, for example, by applying hot-vapor filtration or addition of viscosity-reducing solvents such as methanol or mixture of methanol and water [33]. Another difficulty associated with the use of bio-oils in any combustion systems is its low pH value, which could cause a serious corrosion problem. This problem may be alleviated by blending the bio-oil in appropriate proportion with diesel oil in the form of emulsions with the aid of a surfactant or by converting some acid chemicals via esterification reaction [4,33,34]. Apart from its high viscosity and acidic property, bio-oil from cassava pulp residue is less attractive as a liquid fuel because of its relatively low heating value. Conversion of oxygenated compounds in the oil to obtain higher contents of hydrocarbons via chemical upgrading such as hydrotreating, and catalytic cracking has been recommended to mitigate this shortcoming [31]. Concerning this problem, we have tried another approach by blending the raw bio-oil from cassava pulp residue with its char to produce a slurry fuel. It was found that a slurry with an optimum solid loading of 30 wt% gave increased heating value to about 20 MJ/kg and with the apparent slurry viscosity of 300 mPas at 100 s^{-1} shear rate.

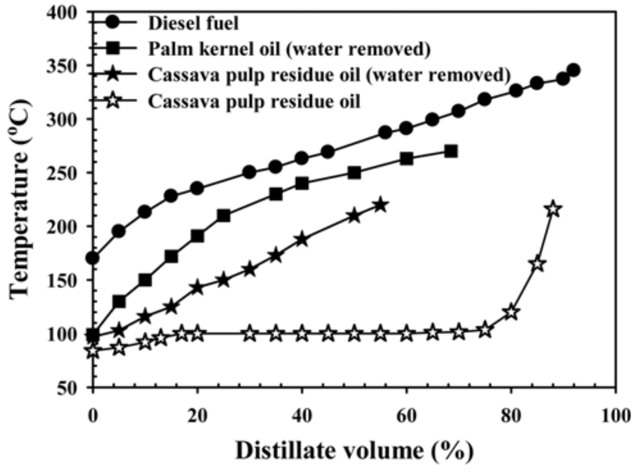


Fig. 7. Distillation curves of diesel and bio-oils derived from pyrolysis of biomasses at 700 °C.

3-2. Chemical Compositions

The dewatered bio-oils were fractionated prior to identification and quantification for their chemical components. Eluted fractions of the two bio-oils derived at the pyrolysis temperatures of 500 and 700 °C are shown in Table 3. Major components of palm kernel cake oil were fractions eluted by diethyl ether, consisting of oxygenated compounds such as phenols, acids, esters, etc. On the other hand, the main fraction of cassava pulp residue oil was that eluted by methanol, representing polar and/or non-volatile compounds. The amount of bio-oil fraction eluted by pentane was lowest, which consisted

Table 3. Chemical fractionations of bio-oils

Bio-oil fraction	Weight%			
	Palm kernel cake		Cassava pulp residue	
	500 °C	700 °C	500 °C	700 °C
Pentane	3.69	3.97	3.11	1.97
Toluene	8.67	11.70	2.88	4.32
Diethyl ether	58.37	48.40	15.40	13.84
Methanol	29.23	30.06	56.79	58.86
Total	99.96	94.13	78.18	78.99

Table 4. Hydrocarbon compounds of bio-oils derived at two different pyrolysis temperatures

Chemical	Chemical concentration in bio-oil (wt%)			
	Palm kernel cake		Cassava pulp residue	
	500 °C	700 °C	500 °C	700 °C
n-Octane, C_8	2.786	2.415	2.312	1.134
1,4-Dimethyl-cyclohexane	0.195	0.112	0.810	0.075
Methyl-cycloheptene	0.058	0.218	0.000	0.062
1,3-Dimethyl-cyclohexane	0.000	0.008	0.000	0.021
Ethyl-cyclohexane	0.000	0.004	0.000	0.014
n-Nonane, C_9	0.011	0.041	0.005	0.015
n-Decane, C_{10}	0.017	0.014	0.002	0.000
n-Undecane, C_{11}	0.220	0.073	0.012	0.005
n-Dodecane, C_{12}	0.025	0.028	0.000	0.000
n-Tridecane, C_{13}	0.085	0.070	0.008	0.000
n-Tetradecane, C_{14}	0.068	0.061	0.004	0.007
n-Pentadecane, C_{15}	0.052	0.149	0.023	0.029
n-Hexadecane, C_{16}	0.055	0.038	0.012	0.057
n-Heptadecane, C_{17}	0.026	0.190	0.072	0.114
n-Octadecane, C_{18}	0.012	0.007	0.026	0.043
n-Nonadecane, C_{19}	0.043	0.017	0.011	0.221
n-Eicosane, C_{20}	0.023	0.020	0.006	0.011
n-Docosane, C_{22}	0.026	0.017	0.005	0.083
n-Tricosane, C_{23}	0.121	0.022	0.005	0.169
n-Tetracosane, C_{24}	0.026	0.028	0.011	0.203
n-Pentacosane, C_{25}	0.078	0.116	0.011	0.279
n-Hexacosane, C_{26}	0.097	0.055	0.047	0.241
n-Heptacosane, C_{27}	0.189	0.137	0.041	0.053
n-Octacosane, C_{28}	0.190	0.102	0.017	0.207
n-Nonacosane, C_{29}	0.000	0.123	0.013	0.232
n-Triacontane, C_{30}	0.000	0.048	0.018	0.222
n-Hentriacontane, C_{31}	0.000	0.179	0.013	0.109
n-Dotriacontrane, C_{32}	0.000	0.718	0.019	0.119
n-Tritriacontane, C_{33}	0.000	0.134	0.000	0.073
n-Tetratriacontane, C_{34}	0.000	0.022	0.000	0.000
Alkanes (unknown)	0.000	0.006	0.061	0.312
Total of alkanes	4.403	5.172	3.564	4.11
Total of alkenes (unknown)	0.133	0.143	0.005	0.010
Benzene	0.658	0.710	0.430	0.341
Toluene	0.568	0.342	1.933	0.432
Ethylbenzene	0.187	0.154	0.582	0.066
Xylene	0.122	0.540	0.169	0.014
Styrene	0.094	0.076	0.000	0.010
1-Methylethyl-benzene	0.044	0.033	0.000	0.022
n-Propylbenzene	0.025	0.019	0.000	0.000
1,2,3-Trimethylbenzene	0.000	0.021	0.000	0.000
Isopropylbenzene	0.000	0.004	0.000	0.005
2-Propenyl-benzene	0.080	0.032	0.000	0.000
1-Propyne-3-phynyl	0.080	0.070	0.000	0.016
Indene	0.008	0.022	0.000	0.000
Butyl-benzene	0.006	0.000	0.000	0.000
Pentyl-benzene	0.009	0.000	0.000	0.000
Benzene cyclohexyl	0.011	0.377	0.216	0.054
3-Methylpentyl-benzene	0.024	0.000	0.000	0.000
1,2,3,4-Tetrahydro-1,4-dimethyl-naphthalene	0.024	0.080	0.000	0.030
Octyl-benzene	0.019	0.000	0.000	0.000
Bibenzyl	0.000	0.007	0.004	0.004
Phenanthracene	0.000	0.030	0.000	0.032
Total of aromatics	1.959	2.517	3.334	1.026
Total of hydrocarbons	6.495	7.832	6.902	5.146

mainly of alkanes and light aromatic compounds. The fraction eluted by toluene comprised the aromatic compounds and high molecular weight alkanes. Palm kernel cake oil gave higher content of pentane and toluene fractions as compared to the oil derived from cassava pulp residue. On the effect of pyrolysis temperature, at higher pyrolysis temperature of 700 °C both oils gave higher content of toluene fraction but lower content of diethyl ether fraction and approximately the same amount of methanol fraction compared to the condition at the lower temperature of 500 °C. Increasing pyrolysis temperature from 500 to 700 °C tended to decrease the pentane fraction of the oil derived from cassava pulp residue, whereas pyrolysis temperature exerted almost no effect for the case of kernel cake derived oil.

Table 4 shows the hydrocarbon compounds present in the two bio-oils obtained at pyrolysis temperatures of 500 and 700 °C. The analysis results show that the hydrocarbons in bio-oils consisted of n-paraffins, aromatics and small amount of olefins. Alkanes were distributed in the range of C_8-C_{34} with the highest concentrations of n-C_8 being detected. This agrees with the previous works for slow pyrolysis of various biomasses [23,35,36] which reported that pentane fraction consisted of normal alkanes in the range of C_7-C_{33}. The content of normal octane (n-C_8) in the palm kernel cake oil remained practically unchanged at the two pyrolysis temperatures studied, but lower concentration of n-C_8 was observed at the higher temperature of 700 °C for liquid product of cassava pulp residue. At the lower pyrolysis temperature of 500 °C, C_8-C_{28} alkanes were observed for kernel cake derived oil, while cassava pulp residue oil yielded C_8-C_{32} alkane fraction. However, increasing of C_{14}-C_{34} content was detected in both bio-oils at the higher pyrolysis temperature of 700 °C. This could result from polymerization of low molecular weight alkanes, giving high molecular weight products at this high temperature condition [24]. Moreover, loss of hydrogen radicals in the long chain alkane could further produce alkenes at higher cracking temperature [37]. In this study, a definite increasing of alkene yield was observed for cassava pulp residue oil with increased py-

Table 5. Oxygenated compounds of bio-oils derived at two different pyrolysis temperatures

Chemical	Chemical concentration in bio-oil (wt%)			
	Palm kernel cake		Cassava pulp residue	
	500 °C	700 °C	500 °C	700 °C
2,3-diol-p-dioxane	0.898	2.077	5.646	3.415
Furfural	0.143	0.466	0.000	0.432
3-Furanmethanol	0.792	1.610	0.482	0.436
2-Methyl-2-cyclopenten-1-one	0.082	0.134	0.040	0.048
1-(2-Furanyl)-ethanone	0.080	0.243	0.068	0.028
Cyclohexanone	0.000	0.000	0.076	0.023
Benzaldehyde	0.308	0.822	0.667	0.689
2-Furanmethanol-acetate	0.015	0.094	0.026	0.000
2,5-Dihydro-3,5-dimethyl-2-furanone	0.257	0.356	0.082	0.031
2-Hydroxy-3-methyl-1-cyclopenten-1-one	0.180	0.326	0.000	0.391
3-Ethyl 2-hydroxy-2-cyclopenten-1-one	0.099	0.076	0.203	0.068
2-Methyl-benzofuran	0.026	0.024	0.000	0.000
1,2,4-Trimethoxybenzene	0.830	0.998	0.000	0.000
Verapamil	0.000	0.000	0.000	2.405
Total of ethers, ketones and aldehydes	3.710	7.226	7.290	7.966
Benzoic acid	0.000	0.650	0.000	0.000
Octanoic acid (Caprylic acid)	0.714	0.688	0.000	0.000
Decanoic acid (Capric acid)	0.999	1.094	0.000	0.000
Dodecanoic acid (Lauric acid)	9.446	6.933	0.028	0.876
Tetradecanoic acid (Myristic acid)	3.271	2.093	0.000	0.491
Hexadecanoic acid (Palmitic acid)	1.394	1.410	0.000	0.499
(9Z)-Octadecenoic acid (Oleic acid)	2.106	1.456	0.000	0.246
Octadecanoic acid (Stearic acid)	0.168	0.473	0.000	0.140
Total of acids	18.098	14.797	0.028	2.252

rolysis temperature, whereas palm kernel cake oil showed a slight increasing of alkenes but a much higher alkene content than that derived from cassava pulp residue oil. For aromatic group, the major aromatic compounds identified were benzene, toluene, ethylbenzene and xylene. Polycyclic aromatic hydrocarbons (PAH), which are a group of two or more fused aromatic rings, were also detected in the bio-oil products. Several PAHs are carcinogens such as benz[a] anthracene, benzo[a]pyrene and dibenz[a,h]anthracene [38]. However, some PAHs such as naphthalene and its derivatives can be used in leather tanning to solve the problem of harmful insects, while indene is used to produce indene/cumarone thermoplastic resins [39]. In this study, some PAHs including indene, naphthalene, 1,2,3,4-tetrahydro-1,4 dimethyl and phenanthracene were detected and the amounts were increased at higher temperature of 700 °C. This agrees with the work of Nugranad [10] who reported the significant increase of single aromatics and PAH concentrations with increasing in pyrolysis temperature from 450 to 600 °C. They hypothesized that the presence of aromatics and PAH at the higher temperature of 600 °C could result from the polymerization and aromatization of alkenes and/or decomposition of lignin to give mono and polycyclic aromatics at this high temperature. However, the opposite trend of decreasing content of single aromatics with increasing of pyrolysis temperature was observed for cassava pulp residue oil in this study. In addition, the high molecular weight of PAHs or some carcinogen chemicals were not detected by GC/MS in this study; it is likely that they could present in the form of non-volatile compounds in the methanol fraction that could not be directly analyzed.

Chemical compositions of oxygenated compounds are illustrated in Table 5. There are about 50 different types of chemical species that could be identified, including phenolic compounds, ethers, esters, acids, some species of furans, etc. For kernel cake derived oil, acids (n-C_8-C_{18}) and esters are the major oxygenated compound amounting to 14.80-18.10 wt% and 14.94-19.69 wt%, respectively. It may be possible that the high content of free fatty acids derived from palm kernel oil could come from the remaining extracted oil present in the original biomass feedstock, which contains high content of lauric acid, myristic acid, palmitic acid and oleic acid. Oil from cassava pulp residue showed much lower concentration of acids (0.03-2.25 wt%) and esters (0.17-2.11 wt%) but with dominant contents of ethers, ketones and aldehydes (7.29-7.97 wt%). In addition, palm kernel cake oil obviously had higher concentration of phenolics and alcohols (9.26-14.17 wt%) such as cresol, guaiacol, eugenol, and syringol than those obtained with cassava pulp residue oil (3.06-3.88 wt%). It is probable that higher lignin content in palm kernel cake could be responsible for the increase of these compounds, as they were produced by the cracking of phenyl-propane unit of lignin structure [12,40]. It has been reported in some studies that phenol content increased continuously with increasing pyrolysis tempera-

Table 5. Continued

Chemical	Chemical concentration in bio-oil (wt%)			
	Palm kernel cake		Cassava pulp residue	
	500 °C	700 °C	500 °C	700 °C
Benzyl alcohol	0.281	0.233	0.000	0.109
Phenol	2.747	2.010	1.643	0.291
2-Methyl-phenol (o-Cresol)	0.000	0.000	0.113	0.042
4-Methyl-phenol (p-Cresol)	0.498	0.600	0.235	0.066
2-Methoxy-phenol (Guaiacol)	0.000	0.482	0.229	0.156
2,3-Dimethyl-phenol	0.086	0.000	0.000	0.000
3,4-Dimethyl-phenol	1.136	0.247	0.051	0.000
2-Methoxy-4-methyl-phenol	0.624	0.451	0.144	0.000
1,2-Benzenediol	0.657	0.722	0.307	0.170
4-Ethyl-4-methoxy-phenol	0.950	1.181	0.142	0.832
Benzenepentanol	0.000	0.000	0.007	0.000
4-Methyl-1,2-benzenediol	0.562	0.467	0.000	0.000
2-Methoxy-4-vinylphenol (Eugenol)	0.531	0.664	0.000	0.468
2,6-Dimethoxy-phenol (Syringol)	0.961	1.360	0.081	0.033
4-Methyl-1,3-benzenediol	0.000	0.531	0.000	0.000
2-Methoxy-4-(1-propenyl)-phenol	0.000	0.298	0.035	0.000
2-Methoxy 6-(2-propenyl)-phenol	0.000	0.298	0.000	0.000
Methylparaben	0.000	0.200	0.000	0.000
2,5-Bis(1,-dimethylethyl)-phenol	0.000	0.293	0.000	0.075
2,6-Dimethoxy-4-(2-propenyl)-phenol	0.230	0.117	0.000	0.000
2,6-Dimethoxy-4-(2-propenyl)-phenol	0.000	2.307	0.000	0.000
2,4,6-Tris(1,1 dimethyl ethyl)-phenol	0.000	1.632	0.000	0.040
2-(1,1-Dimethylethyl)-4(1-methyl-1-phenylethyl)-phenol	0.000	0.000	0.000	0.108
2,6-Bis(1,1-dimethylethyl)-4-(1-1methyl)-1-phenylethyl)-phenol	0.000	0.000	0.000	0.241
2,2'-Methylene-bis(6-1,1-dimethyl ethyl)-4-methyl-phenol	0.000	0.000	0.000	0.027
2,4-Bis(dimethylbenzyl)-6-t-butyphenol	0.000	0.081	0.077	1.224
Total of alcohols and phenols	9.263	14.174	3.064	3.882
Total of esters	19.688	14.938	2.108	0.172
Total of unknown	13.476	5.103	1.998	0.711
Total oxygenated compounds	64.235	56.238	14.488	14.983

ture [12,41]. However, in this work, a decrease in phenol content was observed at the high pyrolysis temperature (700 °C), and this could result from further reactions of phenol to give higher concentrations of furans, aldehydes and ketones [40]. Furthermore, pyrolysis at the temperature of 700 °C gave rise to a decrease in ester group. This could arise from the hydrolysis of esters to alcohols and acids, followed by their decomposition to CO_2 and H_2 [42]. It is also interesting to note that cassava pulp residue, which contains higher polysaccharides (starch content of 64-70 wt% [43]), should provide high contents of sugars, furans, acetaldehydes and acids [44]. However, these chemical compounds probably exist in too low concentrations to be detected in dewatered cassava pulp residue oil. It may be possible that some of these chemicals presenting in the crude bio-oils may have lost with water during the water removing step, since it has been reported that water soluble fraction of bio-oils contained products derived from hydrolysis and oxidation of glucose such as acetic acid, acetone, alcohols, aldehydes and sugars [45].

The bio-oils derived from pyrolysis of biomasses in the present study provide a source of potential chemical feedstocks such as octane, toluene, benzene, naphthalene, lauric acid, oleic acid, phenol, etc. However, due to their presence in low concentrations, the complete separation of individual specific component is too costly, and it is more logical and practical to utilize them by separating into different fractions having similar chemical properties or by converting the whole bio-oil into useful chemicals, making use of its abundant functional groups [9]. For example, dewatered bio-oil from palm kernel cake contains reasonable amounts of carboxylic acids and phenols which can readily react with lime to form calcium salts and used for efficient capture of acid gases from coal-fired power plants [1]. In addition, phenolic compounds in kernel cake derived oil may be used as partial or total replacement for pure phenol in making phenol-formaldehyde resins after separation via the process of solvent extraction with pH adjustment [46]. The dominant contents of ketone and aldehyde groups in bio-oil from cassava pulp residue could be separated by dissolution into an added water phase which can be used, for example, as a meat browning agents for pro-

Table 6. Properties of chars derived at two different pyrolysis temperatures

Properties	Char product			
	Palm kernel cake		Cassava pulp residue	
	500 °C	700 °C	500 °C	700 °C
Bulk density (g/cm^3) (particle size of 2.03 mm)	0.496	0.523	0.168	0.176
True density (g/cm^3)	1.549	1.784	1.651	1.754
Proximate analysis (Dry basis) (wt%)				
Volatile	28.00	14.61	36.78	29.23
Fixed carbon	60.72	69.08	52.94	56.36
Ash	11.28	16.32	10.28	14.41
Elemental analysis (wt%)				
C	64.28	60.88	58.69	55.30
H	3.33	1.52	2.84	1.65
O	31.21	35.06	38.34	42.48
N	1.18	2.54	0.13	0.57
H/C (mole ratio)	0.62	0.30	0.58	0.36
O/C (mole ratio)	0.36	0.43	0.49	0.58
Calorific value (MJ/kg)	30.57	34.65	28.60	29.28
Porous characteristics				
BET surface area (m^2/g)	NA	209.3	NA	33.6
Micropore area (m^2/g)		185.6		26.9
Average pore size (nm)		2.04		2.58
Total pore volume (cm^3/g)		0.107		0.022
Micropore volume (cm^3/g)		0.089		0.013

NA: not analyzed

viding smoky flavors [1].

4. Char Properties

Characteristics of the chars derived from pyrolysis of the two types of biomass at 500 and 700 °C are listed in Table 6. Bulk densities of the chars derived from pyrolysis at both temperatures were lower than that of the corresponding raw materials (about 40% for cassava pulp residue and 10% for palm kernel cake). A slight increase of bulk and true densities of chars were observed when the pyrolysis temperature was increased from 500 to 700 °C for both materials, mainly because of additional char devolatilization causing particle shrinkage. The main component of chars was fixed carbon being in the range 60.7-69.1 wt% for palm kernel cake and 52.9-56.4 wt% for cassava pulp residue. As expected, higher pyrolysis temperature caused the increase of fixed carbon and a consequent decrease in the volatile content. Comparing the results of elemental analysis in Tables 1 and 6 indicates that the carbon content increased and the amounts of the other elements decreased after pyrolysis. It may be that during pyrolysis, hydrogen and oxygen were consumed via reactions of dehydrogenation and/or deoxygenation to produce CO_2, CO, H_2, H_2O, etc [47]. This should cause the decrease of molar ratio of H/C and O/C in chars. Calorific values of the derived chars tended to increase with increasing the pyrolysis temperature and varied in the range of 29-35 MJ/kg which is comparable to that of coal (~35 MJ/kg) [48].

Porous characteristics of the produced chars after pyrolysis at 700 °C are shown in Table 6. The porous properties of chars derived at pyrolysis temperature of 500 °C were not reported here because their N_2 adsorption isotherms could not be measured due to the inaccessibility of N_2 molecule into a not well developed pore structure of this char at low measuring temperature of −196 °C. The results at pyrolysis temperature of 700 °C show that palm kernel cake based char has much higher total pore volume and surface area and consists mainly of microporosity (83.2%), while the cassava pulp residue based char possesses lesser proportion of micropores (59.1%) and larger average pore size. The lower micropore volume of cassava residue char, which results in much lower BET surface area (34 m^2/g) compared to that derived from kernel cake char (209 m^2/g), is hypothesized to result from the differences in their chemical compositions and physical structure. The higher volatile content of cassava pulp residue (Table 1) and its softer and looser structure may facilitate the more rapid and intense release of volatiles, thus creating char structure with relatively larger pore sizes and hence lower surface area and microporosity [49]. The reasonably high microporosity and surface area of kernel cake char indicates that it should have a potential to be further activated to produce highly porous activated carbons.

5. Gas Compositions

Table 7 shows gas yields and compositions obtained from the pyrolysis of biomasses at two different pyrolysis temperatures of 500 and 700 °C. There is almost no difference in total gas yields at 500 and 700 °C for the pyrolysis of both biomasses. Gas yields obtained varies in the range of 19.4-20.9 wt% (0.13-0.17 m^3/kg-biomass) and 31.7-32.4 wt% (0.21-0.27 m^3/kg) for the pyrolysis of palm kernel cake and cassava pulp residue, respectively. The gas product produced from cassava pulp residue pyrolysis gave higher HHV (MJ/kg biomass) than that derived from pyrolysis of palm kernel cake and higher pyrolysis temperature at 700 °C giving higher heating value than at 500 °C. The gas products consist of H_2, CO, CO_2 and CH_4 with CO_2 being the dominant component among the others; 13.2-14.0 wt% for palm kernel cake and 17.1-21.1 wt% for cas-

Table 7. Gas yields of biomass pyrolysis at two different pyrolysis temperatures

Gas component	Gas yield (wt%) (N_2 and H_2O free)			
	Palm kernel cake		Cassava pulp residue	
	500 °C	700 °C	500 °C	700 °C
H_2	0.01	0.25	0.04	0.50
CO	4.31	4.92	9.69	11.06
CO_2	13.97	13.19	21.14	17.12
CH_4	1.13	2.58	1.57	3.04
Total yield (wt%)	19.42	20.94	32.44	31.72
Gas volume (m^3/kg-biomass)	0.13	0.17	0.21	0.27
High heating value (HHV, MJ/kg-biomass)	1.14	2.28	1.90	3.47

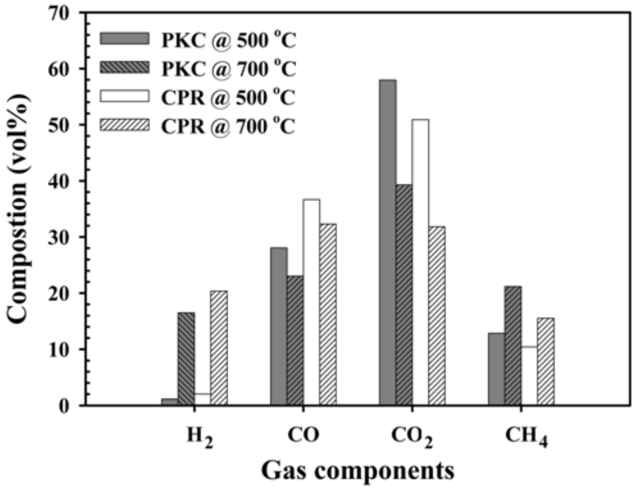


Fig. 8. Gas product compositions from pyrolysis of two biomasses at 500 and 700 °C (PKC: palm kernel cake and CPR: cassava pulp residue).

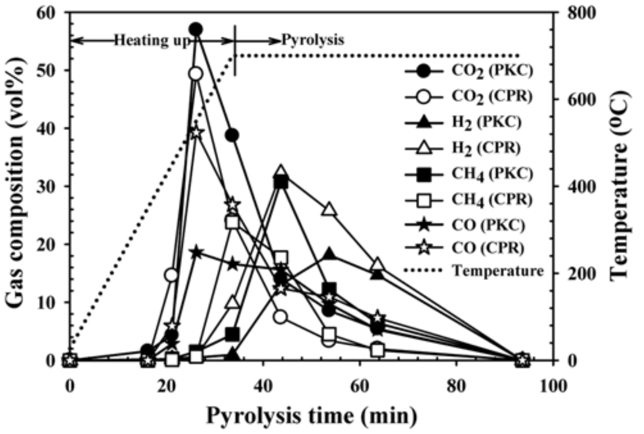


Fig. 9. Gas product distribution versus pyrolysis time derived from pyrolysis of palm kernel cake (PKC) and cassava pulp residue (CPR) at final temperature of 700 °C.

sava pulp residue. Fig. 8 shows gas compositions for the pyrolysis of two biomasses at 500 and 700 °C. Increasing pyrolysis temperature caused a decrease in CO and CO_2 content and an increase in H_2 and CH_4 composition. It is also noted that pyrolysis temperature had a strong influence on H_2 content. It increased from 1.13 to 16.5 vol% for palm kernel cake and 2.03 to 20.36 vol% for cassava pulp residue when the pyrolysis temperature was increased from 500 to 700 °C. Overall, cassava pulp residue gave higher gas yield than palm kernel cake, and this may be attributed to the higher carbohydrate content of cassava pulp residue. Li and co-worker [50] found that biomass components had a direct effect on the product yields; cellulose and hemicellulose can generate higher gas product than that of lignin at the same pyrolysis temperature. Furthermore, the type of biomass feedstock also had a direct bearing on the composition of gas products. In this work, there existed a difference in the compositions of gas product derived from the pyrolysis of each biomass. Pyrolysis of palm kernel cake provided dominant gas component of CO_2 with the highest content of 57.94 vol% being observed at 500 °C. On the other hand, higher syngas content (H_2 and CO) could be observed from cassava pulp residue pyrolysis, especially at pyrolysis temperature of 700 °C where the highest syngas content of 52.7 vol% was achievable. It may be presumed that the higher hydrogen yield from pyrolysis of cassava pulp residue may result from thermal decomposition of its higher cellulose and hemicellulose contents [13]. Moreover, higher O/C molar ratio in cassava pulp residue (Table 1) is indicative of higher content of oxygenated groups such as carboxyl group (-COOH) and ether group (C-O-C) and these groups may decompose to produce more CO in the gas product [13].

Fig. 9 shows gas product distribution at different pyrolysis times for the batch pyrolysis of palm kernel cake and cassava pulp residue at the temperature of 700 °C. It shows that trace amounts of CO_2 and CO were first produced at 350 °C. Then, they rapidly reached the maximum concentration at 550 °C, and afterward their concentration started to decline, which is in accord with the results from previous studies [50,51]. The maximum content of H_2 and CH_4 was produced around 700 °C during the hold time period. Previous works [52-54] have indicated that the production of H_2 at higher temperatures was the result of secondary reactions, possibly due to tar and char cracking and water gas shift reaction. In addition, it was reported that these reactions could also cause the increase or decrease in the content of the other gases (CO, CH_4 and hydrocarbon gases).

CONCLUSIONS

Batch pyrolysis study in a fixed-bed reactor for two types of biomasses, cassava pulp residue and palm kernel cake, showed that pyrolysis conditions including temperature (300-700 °C) and the average particle size in the range of 0.71-2.03 mm greatly influenced the product yields (liquid, gas and char), while N_2 purge rate (50-600 cm^3/min) and heating rate (5-20 °C/min) gave almost insignificant effect. The slow pyrolysis of palm kernel cake and cassava pulp residue gave the maximum liquid yields of 54.3 wt% and 42.4 wt%, respectively. On product characterization, it was discovered that fuel properties and chemical properties of bio-oils, chars and gases depended strongly on biomass type and pyrolysis temperature. It is possible to use dewatered bio-oil from kernel cake pyrolysis as a substitute for petroleum-based fuel because of its relatively high heating value, and having similar boiling range distribution compared to diesel fuel. To fully utilize this bio-oil in a combustion system, however, the problem of its high viscosity and carbon residue and low pH value must be resolved. On the other hand, bio-oil from cassava pulp residue is less attractive for use as a direct fuel. The utilization of this bio-oil in the form of char-bio-oil slurry or as useful bulk chemicals should be a better alternative. The derived chars had reasonably high calorific value (29-35 MJ/kg) comparable to that of coal (~35 MJ/kg), and palm kernel cake char showed good promise as a precursor for further production of activated carbon due to its relatively high BET surface area of about 209 m^2/g. The produced gas from biomass pyrolysis offered relatively low heating values in the range of 1.14-3.47 MJ/kg biomass but could be used as a fuel to supply heat for the pyrolysis process itself.

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