Fast pyrolysis of palm kernel shells: Influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds

3 authors, including:

Su-Hwa Jung
Korea Institute of Industrial Technology

22 PUBLICATIONS **371** CITATIONS

SEE PROFILE

Joo-Sik Kim
University of Seoul

49 PUBLICATIONS **874** CITATIONS

SEE PROFILE

Fast pyrolysis of palm kernel shells: Influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds

Seon-Jin Kim, Su-Hwa Jung, Joo-Sik Kim *

Faculty of Environ. Eng., Univ. of Seoul, 90 Jeonnong-Dong, Dongdaemun-Gu, Seoul 130-743, Republic of Korea

ARTICLE INFO

ABSTRACT

Palm kernel shells were pyrolyzed in a pyrolysis plant equipped with a fluidized-bed reactor and a char-separation system. The influence of reaction temperature, feed size and feed rate on the product spectrum was also investigated. In addition, the effect of reaction temperature on the yields of phenol and phenolic compounds in the bio-oil was examined. The maximum bio-oil yield was 48.7 wt.% of the product at 490 °C. The maximum yield of phenol plus phenolic compounds amounted to about 70 area percentage at 475 °C. The yield of pyrolytic lignin after its isolation from the bio-oil was approximately 46 wt.% based on the water and ash free oil. The pyrolytic lignin was mainly composed of phenol, phenolic compounds and oligomers of coniferyl, sinapyl and p-coumaryl alcohols. From the result of a GPC analysis, the number average molecular weight and the weight average molecular weight were 325 and 463 g/mol, respectively.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Bio-oil from fast pyrolysis can be used in static applications, such as in boilers, diesel engines for power generation and industrial boilers and kilns to replace fossil fuels. In addition, it can also be a chemical source, with more than 300 organic compounds (Gayubo et al., 2010). Lignin, one of the major components of biomass, has attracted particular attention because of its phenolic nature, from which a wide variety of phenol and phenolic compounds (guaiacol, syringol and their alkylated derivatives) can be derived. Phenol and phenolic compounds are valuable and useful chemicals as a source of phenolic resin (Mohan et al., 2006; Scholze and Meier, 2001; Effendi et al., 2008). At present, phenol can be synthesized from the partial oxidation of benzene, by the cumene process, or by the Raschig–Hooker process. These typical synthesis methods are usually very complex, and the phenol produced by these methods is also expensive.

Oil palm trees are cultivated mainly in Asia for the production of palm oil. In particular, Malaysia and Indonesia account for 90% of the palm oil world export trade (Sumathi et al., 2008). Palm oil is produced in mills from palm fruit via steaming and squeezing processes. One of the main problems in the palm oil processing is managing of the wastes generated during the processes. The world annual production of palm oil residues (empty fruit bunch, trunk, fronds, palm kernel shells and fibers) amounts to 184.6 million tons (Kelly-Yong et al., 2007). These biomasses have high potential of being turned into renewable energy. Several researchers have pyrolyzed palm oil wastes under various reaction conditions to investigate the mechanism of pyrolysis and characteristics of the products. Yang et al. studied the mechanism of palm oil waste pyrolysis in a packed-bed reactor, and found that temperature played an important role in the bio-oil yield and chemical composition (Yang et al., 2004, 2006a,b). Islam et al. investigated the effect of various pyrolysis conditions (the reaction temperature, the feed particle size and the gas flow rate) on the production of bio-oil from palm kernel shells in a fluidized-bed reactor, using nitrogen as a fluidizing medium, and concluded that the maximum bio-oil yield (58 wt.% of biomass feed) was obtained at a reaction temperature of 500 °C with a particle size of 212–425 μm (Islam et al., 1999). Li et al. pyrolyzed palm kernel shells in a fluidized-bed reactor and reported that the main components of the bio-oil were phenolic compounds (Li et al., 2007).

In this study, palm kernel shells were pyrolyzed in a pyrolysis plant composed of a fluidized-bed reactor and a char-separation system consisting of a cyclone and hot filter, with the product gas used as a fluidizing medium. The purpose of this study was to find the effects of reaction parameters (reaction temperature, feed rate and feed size) on the yield and chemical properties of each pyrolysis product (bio-oil, gas and char). In addition, the phenol and phenolic compound contents in the bio-oil were investigated with respect to the reaction temperature, and characteristics of the pyrolytic lignin isolated from the bio-oils were examined.

* Corresponding author. Tel.: +82 2 2210 5621; fax: +82 2 2244 2245.
E-mail address: joosik@uos.ac.kr (J.-S. Kim).

Table 1
Main characteristics of the palm kernel shells.

Proximate analysis[a] (wt.%)		Elemental analysis[b] (wt.%)	
Moisture	9.4	Carbon	44.56
Volatile matter	82.5	Hydrogen	5.22
Fixed carbon	1.4	Nitrogen	0.4
Ash	6.7	Sulfur	0.05
		Oxygen[c]	49.77
		HHV (MJ/kg)	15.6
Alkali and alkaline earth metal (ppm)		Chemical composition[b] (wt.%)	
Na	178.5	Cellulose	33.04
K	2500	Hemicelluloses	23.82
Mg	875	Lignin	45.59
Ca	16450	Extractives	9.89

[a] Wet basis.
[b] Ash free.
[c] Calculated by difference.

2. Methods

2.1. Feed material

The palm kernel shells used in the experiments were originally imported from Malaysia, and are widely used as a fuel in boilers in Korea. They were first ground and sieved to reduce their particle size to 425–850 μm. The main characteristics of the feed material are listed in Table 1. The proximate analysis showed moisture and volatile matters of 9.4 and 82.5 wt.%, respectively. Elemental analyses showed that the feed material consisted mainly of carbon and oxygen, but that the nitrogen and sulfur contents were very low. The higher heating value of the feed material was 15.6 MJ/kg, calculated using the Dulong equation. Among the alkali and alkaline earth metals in the feed material, the calcium content was very high. The analysis of the chemical composition showed a remarkably high lignin content, with a value of 45.6 wt.%, compared to the woody biomasses; the lignin content is usually below 30 wt.% (McKendry, 2002).

2.2. Pyrolysis plant

The pyrolysis experiments were performed in a bench-scale plant, with a throughput of up to 1 kg/h, consisting of a feeding system, a fluidized-bed reactor, a char-separation system, a quenching system and a gas-circulating system. The feeding system was equipped with two screw feeders, with variable feed rates, which helped uniformly feed the palm kernel shells. The feed material entered directly into quartz sand, with a diameter of 0.4 mm, used as a bed material. The fluidized-bed reactor, which was indirectly heated by electricity, was made of a sus-304 steel tube, with an inner diameter of 110 mm and a height of 390 mm. The reaction temperature was determined from the average value, which was calculated by three thermocouples in the reactor. The char-separation system consisted of a cyclone and a hot filter designed to capture particles bigger than 10 and 2 μm, respectively. The quenching system was made up of a stainless condenser, two glass condensers and an electrostatic precipitator by which oil and aerosol were caught. The stainless condenser and glass condenser were cooled to 20 and −30 °C using water and ethanol, respectively. Non-condensable gas was recycled using a compressor and was used as the fluidizing medium. During the experiment, some non-condensable gas was sampled, using Teflon gas bags (2 L), at intervals of 5 min to analyze the composition. To regulate the pressure in the plant, the excess gas was burned in a flare stack. A schematic diagram of the pyrolysis plant is shown in Fig. 1.

2.3. TGA and DTG experiments

Prior to the pyrolysis experiments, TGA experiments were carried out with palm kernel shells at various heating rates; 10, 15 and 20 °C/min, using a thermogravimetric analyzer (TGA 2050, TA Instruments). In each experiment, the sample amount was 10–20 mg, with the flow rate of nitrogen gas of 100 ml/min, used as the purging gas. The TGA and DTG curves of the palm kernel shells are shown in Fig. 2.

As shown in Fig. 2(a) and (b), the first weight loss of the feed material occurred at 100 °C, due to the moisture evaporation. The
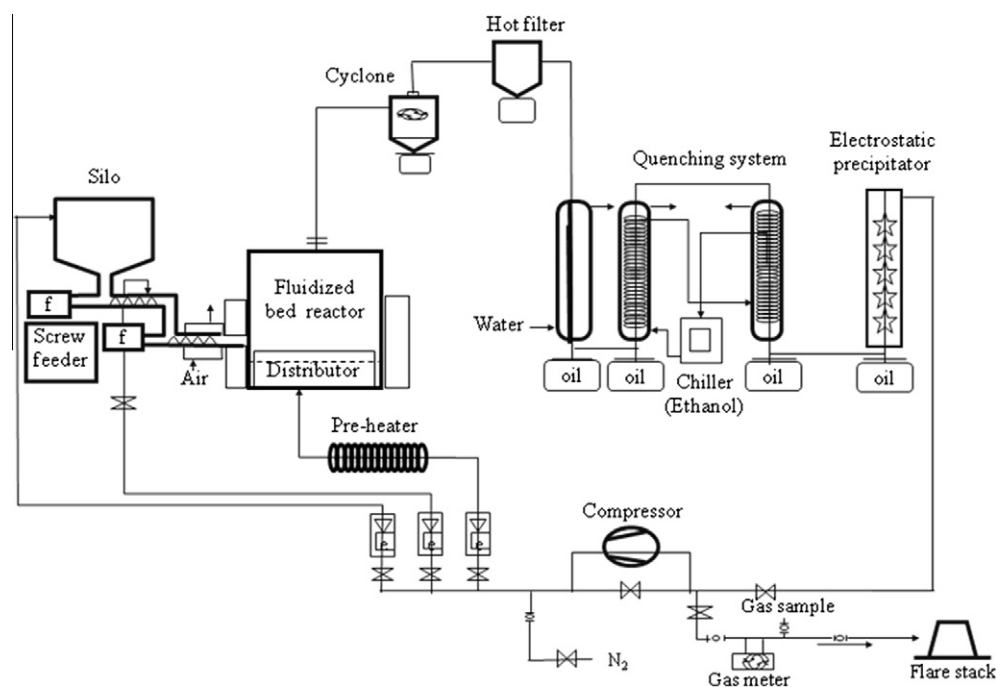

Fig. 1. Schematic diagram of the pyrolysis plant (This figure shows the details of the pyrolysis system.)
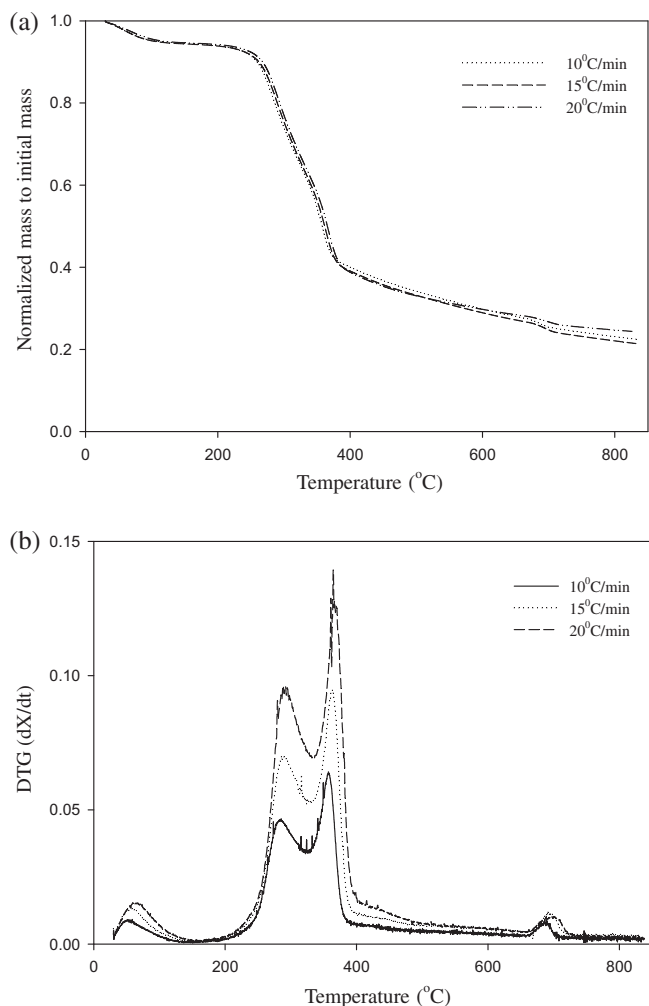
Fig. 2. TGA (a) and DTG (b) curves for palm kernel shells (This shows the thermal degradation characteristics of the palm shells.)

second weight loss took place at 200–400 °C, due to hemicelluloses and cellulose decomposition. The decomposition of lignin takes place over a broad temperature range. It is difficult to separate the decomposition range among hemicellulose, cellulose, and lignin completely. It seemed, however, that the weight loss above 400 °C was mainly due to the decomposition of lignin; the decomposition rate was low until 800 °C, compared to the region between 230 and 400 °C. The minimum pyrolysis reaction temperature was determined to be 430 °C, as most of hemicelluloses and cellulose seemed to be decomposed at this temperature; the decomposition rate above 430 °C was relatively low.

2.4. Reaction conditions

Pyrolysis experiments were conducted to investigate the influence of reaction temperature on the product yields, in the range

from 430 to 540 °C. Additional experiments were also carried out with different feed sizes and feed rates. In each experiment, the input of the feed material was 350 g, with 3.8 kg of quartz sand was used as the fluidized-bed material. In all the experiments, the product gas was used as the fluidizing medium. The feed material was dried in a drying oven at 105 °C for 24 h to remove the free moisture. The reaction conditions are shown in Table 2. Experiments R1–R6 were performed to investigate the influence of the reaction temperature, with R7 and R8 were comparisons to R4 to find the influence of the feed size and the feed rate, respectively. The calculated residence time of the product vapor in the reactor was around 0.5 s in each of the experiments. Some of the experiments were performed several times to obtain better results.

2.5. Analysis of product

After the pyrolysis experiments, oil, gas and char were obtained. The carbon, hydrogen, nitrogen and sulfur contents in the bio-oils were determined with an elemental analyzer (EA1112, CE Instrument). The water content of bio-oils was analyzed using a Karl Fischer titrator (Metrohm 870, KF Titrino), with HYDRANAL Composite 5 K (Riedel–de Haen) as the titration reagent and HYDRANAL Working Medium K (Riedel–de Haen) as the titration solvent. The higher heating value and the pH of bio-oils were measured by a bomb calorimeter (Model 1261, Parr) and pH meter (Seven Easy pH meter, Mettler Toledo), respectively. The solid content of the bio-oils was defined as the ethanol-insoluble matter when filtered through a membrane filter (Milipore Co., 0.1 μm, polycarbonate). The ash content of the bio-oils was determined by measuring the residue after a sample of bio-oil was ignited overnight in a muffle furnace at 850 °C. The alkali and alkaline earth metals contents were determined with an ICP-AES (ICPE-9000, Shimadzu). The bio-oils produced in the pyrolysis experiments were analyzed quantitatively and qualitatively with a GC–MS (5975C, Agilent), using a HP-5MS capillary column, with helium as the carrier gas. For reliable and accurate quantitative analysis of the bio-oil, relative response factor (RRF) should be determined and applied for various chemicals in the bio-oil. To calculate RRF for each chemical, however, demand tremendous efforts. In the experiments, the area (%) of a GC-chromatogram was used for quantification, because it is considered as a good indication of the amount of GC-detectable compounds in the bio-oils (Park et al., 2008). The gas chromatography unit (7890A, Agilent), equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID), with used argon as the carrier gas, was used to qualitatively analyze the gas components of the pyrolysis gases. The columns employed were a Carboxen-1000 for TCD and HP-plot Al_2O_3/KCl for FID. A Micro/Mesopore and surface area analyzer (ASAP2010, Micromeritics Instrument CO) was used to investigate the surface area of the char. The molecular weight distribution of pyrolytic lignin was analyzed by gel permeation chromatography (Waters GPC system), using a Sepax GPC Mono-300 column. For the GPC, a portion of pyrolytic lignin was dissolved in tetrahydrofuran and then filtered (Target® 0.45 μm NYLON filter). A differential refractometer was used as a detector, with polystyrene used as the standard reagent.

Table 2
Reaction conditions.

Parameter	R1	R2	R3	R4	R5	R6	R7	R8
Reaction temperature (°C)	435	453	475	490	512	533	491	492
Feed size (mm)	0.64	0.64	0.64	0.64	0.64	0.64	0.93	0.64
Feed rate (g/min)	10	10	10	10	10	10	10	5
Flow rate (nL/min)	69	67	65	63	62	60	63	63

2.6. Separation of pyrolytic lignin (water-insoluble fraction)

About 10 g of bio-oil was very slowly dropped into 500 ml of ice-cooled distilled water, while stirring at 6000 rpm using an ultra turrax. About 1 h later, in order to separate the pyrolytic lignin, the suspension was filtered through a membrane filter (Milipore Co., 0.1 μm, polycarbonate). The water-insoluble fraction was dried in a vacuum oven at room temperature for 24 h (Scholze et al., 2001).

3. Results and discussion

3.1. Influence of reaction temperature

After pyrolysis in the plant, gas, oil, and char were obtained in fractions. In each experiment, an organic mass balance was established. In the organic mass balance, the gas yield was calculated from the data on the gas volume produced in the experiments and the gas density obtained from the gas composition. The oil yield was obtained via weighing after the pyrolysis, and then the water and ash contents in it were subtracted from the total oil weight. Finally, the char obtained in the experiments was burnt in a furnace to obtain the organic mass. With fluidized-bed pyrolysis, several factors influence the mass balance of the product, such as the temperature, feed rate and feed size. It is well-known that the most significant of these factors is the reaction temperature. The influence of temperature on the product distribution is presented in Fig. 3.

With increasing temperature up to 490 °C, the bio-oil yield increased and reached 48.7 wt.% of the product. Above 490 °C, the oil yield decreased and; in contrast, the gas yield increased due to the enhanced secondary cracking reactions of the pyrolysis vapors. At 435 °C, the maximum char yield was obtained, mainly due to the incomplete decomposition of the feed material. Due to the enhanced decomposition in the region of 435–490 °C, the char yield decreased gradually, and then slightly increased from 490 °C, indicating that active char-forming secondary reactions were taking place.

3.2. Influence of other parameters

Fig. 4 shows the effects of feed size and feed rate on the product distribution.

Fig. 4 (a), the comparison between R4 (0.425–0.85 mm) and R7 (0.85–1 mm), shows the influence of the feed size on the product
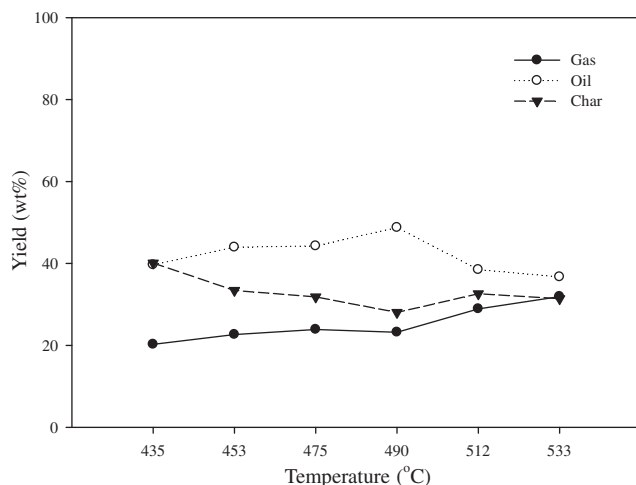

Fig. 3. Influence of reaction temperature on the product distribution (This shows the influence of temperature on the production of gas, char and bio-oil.)
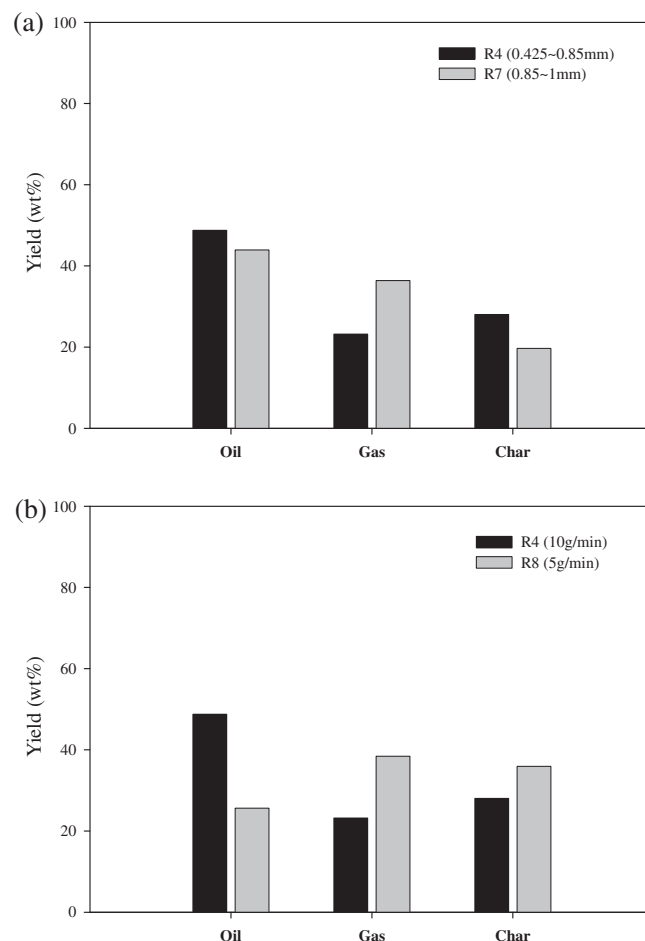

Fig. 4. Influence of (a) feed size and (b) feed rate (This shows the influence of the feed size and feed rate on the product distribution.)

distribution. A smaller feed size led to a higher oil yield. This resulted from the good heat transfer to the inner side of the feed when a smaller amount of feed was used. Fig. 4 (b), the comparison between R4 (10 g/min) and R8 (5 g/min), presents the effect of feed rate on the product yields, and a higher feed rate led to a higher oil yield and lower gas yield because the higher feed rate caused a higher generation of pyrolysis vapors, which led to the short residence time of the pyrolysis vapors in the reactor, consequently preventing secondary cracking reactions.

3.3. Bio-oil

Table 3 represents the main characteristics of the bio-oil obtained from R4.

In all the experiments, the bio-oils consisted of a single phase and had a dark brown color. All bio-oil fractions obtained in each condenser and the electrostatic precipitator in each experiment were collected in a container for homogenization, and then a sample was made for the analysis. As seen from the elemental analysis, the bio-oil consisted mainly of carbon and oxygen. The water content in the bio-oil was about 30 wt.% and the higher heating value 17.9 MJ/kg, which was about half that of traditional fuels (Bridgwater, 2004). The pH of the bio-oil was 3.27. The solid and ash contents were both less than 0.1 wt.%, indicating the good performance of the char-separation system. The GC–MS analysis of the bio-oil is shown in Table 4.

The major components of the bio-oil were phenol, guaiacol, syringol, dimazine, furfural and acids. In particular, the phenol

Table 3
Characteristics of bio-oil.

Items	Run4 (490 °C)
Elemental analysis (wt.%)	
C	47.6
H	8.1
N	0.6
S	–
O[a]	43.7
Water content (wt.%)	30
HHV (MJ/kg)	17.9
pH	3.27
Solid content (wt.%)	0.1
Ash content (wt.%)	<0.1

[a] Calculated by difference.

Table 4
Main compounds of the bio-oil from R4.

Components	Area (%)
Acetic acid	5.46
Furfural	3.42
Phenol	22.1
p-Cresol	1.32
o-Guaiacol	3
Creosol	2.1
Catechol	3.67
3-Methoxy-1,2-benzenediol	1.64
Homocatechol	1.55
Vinylguaiacol	1.97
Syringol	4.09
Iso-eugenol	1.34
Methoxyeugenol	3.09
o-Cresol	1.07
3-Methyl-1,2-benzenediol	1.3
4-Hydroxy-benzoic acid	0.44
2-Methoxy-benzeneethanol	1.01
1,2,4-Trimethoxybenzene	4.51
Methylparaben	1.13
4-Ethyl-1,3-benzenediol	0.8
1,2,4-Benzenetriol	0.27
3-Hydroxy-benzoic acid	0.23
Propanoic acid	0.74

Fig. 5. Yields of phenol and phenolic compounds, with respect to reaction temperature (This shows the influence of temperature on the production of phenols.)

vigorous reactions with other compounds in the pyrolysis vapors between those temperatures. On the other hand, the amount of phenolic compounds was highest at 475 °C. No obvious trend was observed in the yield of phenolic compounds with respect to reaction temperature.

3.4. Product gas and char

The product gas mainly consisted of carbon monoxide, carbon dioxide, hydrogen and other minor hydrocarbons. High reaction temperatures led to higher CO and $C_1–C_4$ hydrocarbon contents and a lower CO_2 content, due to the secondary cracking of volatiles, followed by the reduction of CO_2 to produce CO and CH_4. The higher heating value of the product gas was approximately 4–8 MJ/kg. The char obtained during the experiments had the higher heating value of around 12 MJ/kg. The BET (Brunauer–Emmett–Teller) surface area of the char obtained during the experiments was very small, within the range 2–4 m^2/g.

3.5. Alkali and alkaline earth metal contents of bio-oil and char

The alkali and alkaline earth metals in the bio-oil have a detrimental influence on its storage due to the catalytic effect (Fahmi et al., 2008). Table 5 indicates the distribution of alkali and alkaline earth metals in the bio-oil and char obtained during the experiments. The bio-oil had very low concentrations of alkali and alkaline earth metals compared to the product char. The alkali and alkaline earth metal contents in the bio-oil obtained during the experiments, however, was higher than that of the bio-oil produced in the same system (Jung et al., 2008). This may be due to the higher alkali and alkaline earth metal contents in the palm kernel shells.

and phenolic compound contents in the bio-oil were very high compared to bio-oils obtained from other biomasses (Tsai et al., 2007; Lu, 2008; Yanik et al., 2007). The higher yield of phenol (~22 area percentage in the GC–MS analysis) and phenolic compounds in the bio-oil (R4) may be mainly due to the high lignin content of the palm kernel shells. The high amount of phenol in the bio-oil is of interest, because the use of phenol from the bio-oil after isolation would suggest an alternative to petroleum-based phenol. In addition, the direct use of the bio-oil containing a high amount of phenol would facilitate the synthesis of phenolic resins due to its higher reactivity, compared to other methoxylated or alkylated phenolic compounds.

In Fig. 5, shows the effect of the reaction temperature on the yields of phenol and phenolic compounds.

With increasing temperature up to 475 °C, the total yield of phenol plus phenolic compounds increased, amounting to about 70% bio-oil. Above 475 °C, the total yield decreased. Focusing only on the phenol yield, an increase was observed from 435 to 453 °C, a decrease from 453 to 475 °C, almost no variation from 475 to 512 °C, and a decrease from 512 to 533 °C. From 435 to 453 °C, the lignin portion of palm kernel shells seemed to be gradually pyrolyzed to give a higher phenol yield. The decrease from 512 to 533 °C indicates the possibility of decomposition of phenol or

Table 5
Distribution of alkali and alkaline earth metals in bio-oil and char.

Alkali and alkaline earth metals (ppm)	R4 (490 °C)	
	Oil	Char
Na	129	595
Mg	47	2360
K	236	11050
Ca	635	52500

Table 6
Elemental analysis of the pyrolytic lignin (R1).

Elemental analysis (wt.%)	Water insoluble	Bio-oil
C	74.09	47.6
H	10.69	8.1
N	2.17	0.6
S	–	–
O[a]	13.05	43.7

[a] Calculated by difference.

3.6. Pyrolytic lignin (water-insoluble fraction)

Reactive components for phenolic resin synthesis can be obtained by fractionation of pyrolysis oils. The isolated water-insoluble fraction is pyrolytic lignin. A typical yield of pyrolytic lignin from a wood derived bio-oil is between 14 and 28 wt.%, based on water free bio-oil, and the color of the pyrolytic lignin varies between light and dark brown (Scholze and Meier, 2001). In the experiments, pyrolytic lignin was isolated from bio-oils by the mixing with cold water, and that yielded from the bio-oil of R1 was about 46 wt.% based on water free oil, and was dark brown color. The yield of pyrolytic lignin was much higher than those from other experiments due to the higher lignin content of the palm kernel shells. The water-insoluble (pyrolytic lignin) and water-soluble (remainder) phases were analyzed using a GC–MS system. Phenol has a limited solubility in water (8.3 g/100 ml) at 20 °C. Therefore, in the analysis, phenol was detected with similar contents in both phases. The pyrolytic lignin composed mainly of high molecular weight compounds contained simple phenolic compounds in abundance. The whole bio-oil or the pyrolytic lignin separated in the experiment would be used for phenol–formaldehyde resin, because of a high content of phenol and phenolic compounds in them. Table 6 represents the elemental analysis of the pyrolytic lignin.

For comparison, the elemental composition of the whole bio-oil is also presented in Table 6. The pyrolytic lignin contained more carbon than the whole bio-oil. The hydrogen content of the pyrolytic lignin was comparable to that of the whole bio-oil. The pyrolytic lignin had less oxygen than the whole bio-oil (13.1 wt.% in pyrolytic lignin, versus 43.7 wt.% in whole bio-oil).

Fig. 6 shows the molecular weight distribution of the pyrolytic lignin calculated using gel permeation chromatogram (GPC). As can be seen from Fig. 6, the pyrolytic lignin mainly consisted of higher molecular weight compounds, which cannot usually be de-
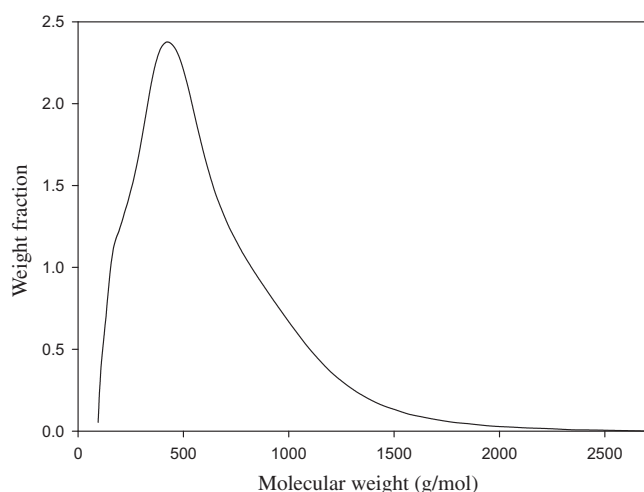
tected by gas chromatography. The number average molecular weight (Mn) and the weight average molecular weight (Mw) were 325 and 463 g/mol, respectively. The molar mass of the elugrams maximum (Mp) was 436 g/mol. The average molecular weights, Mw and Mn, of the pyrolytic lignin were smaller than those of the pyrolytic lignin obtained from woody biomass (Scholze et al., 2001; Ba et al., 2004). The Mw and Mn values confirm that the pyrolytic lignin obtained during the experiment was mainly composed of dimers or trimers of hydroxyphenyl, guaiacyl and syringyl compounds (Bayerbach et al., 2006). Pyrolytic lignins with high fractions of low molecular weight molecules are suitable for condensates with phenol formaldehyde because they are more reactive than high molecular weight molecules (Pizzi, 1994). Polydispersity (Mw/Mn) is a measure of the molecular weight homogeneity of the samples; the pyrolytic lignin had a low polydispersity of 1.4.

4. Conclusions

Palm kernel shells were pyrolyzed in a fluidized-bed reactor. The maximum bio-oil yield occurred at 490 °C, with a value of 49 wt.% of product on the organic-based mass balance. The maximum amount of phenol and phenolic compounds in the bio-oil was about 70 area percentage at 475 °C. The yield of pyrolytic lignin from the bio-oil was obtained at 435 °C; approximately 46 wt.% based on the water free oil. The number average molecular weight (Mn) and the weight average molecular weight (Mw) were 325 and 463 g/mol, respectively. The pyrolytic lignin had a low polydispersity.

References

Ba, T., Chaala, A., Garcia-Perez, M., Rodrigue, D., Roy, C., 2004. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Characterization of water-soluble and water-insoluble fractions. Energ. Fuel 18, 704–712.

Bayerbach, R., Nguyen, V.D., Schurr, U., Meier, D., 2006. Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin): part III. Molar mass characteristics by SEC, MALDI-TOF-MS, LDI-TOF-MS, and Py-FIMS. J. Anal. Appl. Pyrol. 77, 95–101.

Bridgwater, A.V., 2004. Biomass fast pyrolysis. Therm. Sci. 8, 21–49.

Effendi, A., Gerhauser, H., Bridgwater, A.V., 2008. Production of renewable phenolic resins by thermochemical conversion of biomass: a review. Renew. Energ. Rev. 12, 2092–2116.

Fahmi, R., Bridgwater, A.V., Donnison, I., Yates, N., Jones, J.M., 2008. The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. Fuel 87, 1230–1240.

Gayubo, A.G., Valle, B., Aguayo, A.T., Olazar, M., Bilbao, J., 2010. Olefin production by catalytic transformation of crude bio-oil in a two-step process. Ind. Eng. Chem. Res. 49, 123–131.

Islam, M.N., Zailani, R., Ani, F.N., 1999. Pyrolytic oil from fluidised bed pyrolysis of oil palm shell and its characterisation. Renew. Energ. 17, 73–84.

Jung, S.H., Kang, B.S., Kim, J.S., 2008. Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a char separation system. J. Anal. Appl. Pyrol. 82, 240–247.

Kelly-Yong, T.L., Lee, K.T., Mohamed, A.R., Bhatia, S., 2007. Potential of hydrogen from oil palm biomass as a source of renewable energy worldwide. Energ. Policy 35, 5692–5701.

Li, J., Yan, R., Xiao, B., Wang, X., Yang, H., 2007. Influence of temperature on the formation of oil from pyrolyzing palm oil wastes in a fixed bed reactor. Energ. Fuels 21, 2398–2407.

Lu, Z.J., 2008. Pyrolysis oil from fast pyrolysis of maize stalk. J. Anal. Appl. Pyrol. 83, 205–212.

McKendry, P., 2002. Energy production from biomass (part 1): overview of biomass. Bioresour. Technol. 83, 37–46.

Mohan, D., Pittman Jr., C.U., Steele, P.H., 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. Energ. Fuels 20, 848–889.

Park, E.S., Kang, B.S., Kim, J.S., 2008. Recovery of oils with high caloric value and low contaminant content by pyrolysis of digested and dried sewage sludge containing polymer flocculants. Energ. Fuels 22, 1335–1340.

Pizzi, A., 1994. Advanced Wood Adhesives Technology. Marcel Dekker, New York. 219–241.

Scholze, B., Hanser, C., Meier, D., 2001. Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin): part II. GPC, carbonyl groups, and ^{13}C NMR. J. Anal. Appl. Pyrol. 58–59, 387–400.

Scholze, B., Meier, D., 2001. Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part I. PY–GC/MS, FTIR, and functional groups. J. Anal. Appl. Pyrol. 60, 41–54.

Fig. 6. Molecular weight distribution of the pyrolytic lignin (R1) (This shows the molecular weight distribution of a pyrolytic lignin.)

Sumathi, S., Chai, S.P., Mohamed, A.R., 2008. Utilization of oil palm as a source of renewable energy in Malaysia. Renew. Energ. Rev. 12, 2404–2421.

Tsai, W.T., Lee, M.K., Chang, Y.M., 2007. Fast pyrolysis of rice husk: product yields and compositions. Bioresource Technol. 98, 22–28.

Yang, H., Yan, R., Chen, H., Lee, D.H., Liang, D.T., Zheng, C., 2004. Thermogravimetric analysis–fourier transform infrared analysis of palm oil waste pyrolysis. Energ. Fuels 18, 1814–1821.

Yang, H., Yan, R., Chin, T., Liang, D.T., Chen, H., Zheng, C., 2006a. Mechanism of palm oil waste pyrolysis in a packed bed. Energ. Fuels 20, 1321–1328.

Yang, H., Yan, R., Chen, H., Zheng, C., Lee, D.H., Liang, D.T., 2006b. Influence of mineral matter on pyrolysis of palm oil wastes. Combust. Flame 146, 605–611.

Yanik, J., Kornmayer, C., Saglam, M., Yüksel, M., 2007. Fast pyrolysis of agricultural wastes: characterization of pyrolysis products. Fuel Process. Technol. 88, 942–947.