Investigation of operating parameters of water extraction processes for improving bio-oil quality

Boonyawan Yoosuk, Jiraporn Boonpo, Parncheewa Udomsap, and Sittha Sukkasi[†]

National Metal and Materials Technology Center (MTEC), 114 Thailand Science Park,
Phahonyothin Road, Khlong 1, Khlong Luang, Pathumthani 12120, Thailand

Abstract−Water extraction of slow-pyrolysis bio-oil, in order to improve its quality, was investigated in terms of different schemes and operating parameters. The water extraction separated the bio-oil into two phases: an aqueous phase and an organic water-insoluble fraction (or "pyrolytic lignin"). Properties of the pyrolytic lignin extracted with different extraction schemes and conditions were characterized and compared. The results showed that the water temperature and stirring time did not significantly affect the pyrolytic lignin's properties. The water : bio-oil ratio, however, could remarkably reduce the pyrolytic lignin's acidity. Given the findings, an effective time- and resource-saving extraction scheme with appropriate operating conditions could be devised. The resulted pyrolytic lignin, which was essentially the "upgraded" bio-oil, had notably lower acidity, higher heating value, and more stability than the starting bio-oil, due to the removal of alcohols, ketones, carboxylic acids, sugars, ethers, as well as reactive compounds by the water extraction.

Keywords: Pyrolysis, Bio-oil, Water Extraction, Upgrading, Pyrolytic Lignin

INTRODUCTION

With the ever-increasing global demand for energy, alternative bio-fuels such as bio-diesel, bio-ethanol, bio-gas, and bio-oil have gained more research attention, as part of worldwide efforts to search for petroleum-product replacements and to curb global-warming. Bio-oil, also known as pyrolysis oil, pyrolysis liquid, bio-crude oil, wood liquid, wood oil, liquid smoke, wood distillate, pyroligneous acid, and liquid wood, is a liquid product derived from pyrolysis of biomass (combustion of biomass in the absence of oxygen) [1-4]. Bio-oil consists of oxygenated compounds such as water, acids, aldehydes, ketones, phenols, and other complex compounds derived from carbohydrates and lignin [5].

Bio-oil, nonetheless, has several undesirable properties, including high acidity and viscosity, and relative low energy density [6]. These properties are due to the high oxygen content of oxygenated compounds that make bio-oil reactively and thermally unstable. Therefore, upgrading processes, such as chemical upgrading, including catalytic esterification, catalytic hydroprocessing, and catalytic cracking, and physical upgrading, including char removal, hot vapor filtration or distillation, liquid chromatography, centrifugation, liquid filtration, solvent addition, and extraction of organic acids, are needed [2,7-9].

Water extraction, or fractionation, is a relatively simple and inexpensive method that can separate bio-oil into less complex compounds and extract some acidic compounds by using the polarity and solubility in water of the compounds [5,6]. Water extraction of bio-oil can be done by dropping water into bio-oil, or vice versa, while continuously stirring the mixture. During the process, bio-oil is separated into two parts. The first part is a water-soluble fraction (WSF), which is composed of high-polarity compounds, such as formic acid, acetic acid, and ketone. The second part is a water-insoluble fraction (WIF) that is also called pyrolytic lignin, comprising hydrophobic components that originate from lignin [1,9]. Water extraction has been shown to be able to extract 80-90% of polar compound from pyrolysis liquid [6].

In the studies by Ba et al. [1] and Scholze and Meier [10], water extraction of slow-pyrolysis bio-oil was done by dropping water into bio-oil while stirring the mixture. They found that the yield of pyrolytic lignin was in the range of 16-29.6 wt%. The water extraction removed some compounds and improved the pyrolytic lignin's properties. In addition, Vitasari et al. [6] conducted water extraction of fast-pyrolysis bio-oil with stirring speeds up to 600 rpm and water : bio-oil ratios of 0.3 to 0.9. However, the various parameters in the water extraction process have yet to be studied. Therefore, we investigated the effects of various parameters for optimization of the water extraction process for the bio-oil. The properties of pyrolytic lignin derived from different conditions were characterized and compared to the starting bio-oil.

MATERIAL AND METHODS

1. Material

The bio-oil used in this study was produced by Nara Tanka Kogyo Ltd. in Japan, from slow pyrolysis of various wood scraps, e.g., oak, bamboo, sawdust, etc. Among the products that were generated by the process were liquid products comprising bio-oil and wood vinegar, which readily separated from each other at the production facility. The bio-oil part of the liquid products was used in this study. This starting bio-oil had a water content of 4.37 wt%, density of 1.18 g/cm^3 (measured at 15 °C), acidity of 81.38 mg KOH/g oil,

[†]To whom correspondence should be addressed.
E-mail: sitthas@mtec.or.th, sittha@gmail.com

(a)

Bio-oil
↓
Drop bio-oil into water while stirring mixture
↓
Continue to stir
↓
Separate and filter
↓
Wet WIF
↓
Add water & stir for 4 hours
↓
Separate and filter
↓
Wet WIF   **WSF + water**
↓   ↓
Dry at 30°C   Dry at 40°C
↓   ↓
Dry WIF   **WSF**

(b)

Bio-oil
↓
Drop bio-oil into water while stirring mixture
↓
Continue to stir
↓
Separate and filter
↓
Wet WIF   **WSF + water**
↓   ↓
Dry at 30°C   Dry at 40°C
↓   ↓
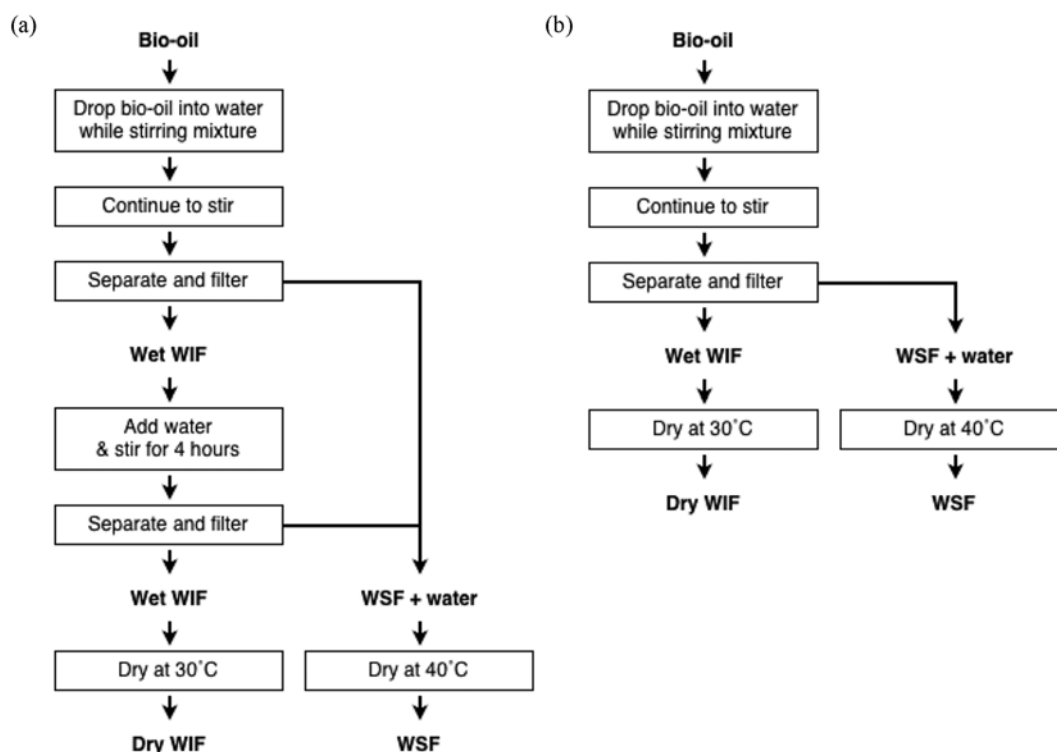**Dry WIF**   **WSF**

Fig. 1. Water extraction methods.

viscosity of 114.5 cP (measured at 40 °C), and heating value of 25.8 MJ/kg. The carbon, hydrogen, nitrogen, and oxygen content was 65.0 wt%, 7.6 wt%, 0.2 wt%, and 27.2 wt%, respectively. The weight-average molecular weight (Mw), number-average molecular weight (Mn), and polydispersity (Mw/Mn) were 665 g/mol, 508 g/mol, and 1.31, respectively.

2. Bio-oil Fractionation

Two schemes of water extraction of bio-oil were adapted from a method reported by Scholze and Meier [10]. The first scheme, shown in Fig. 1 as Method A, involved dropping bio-oil into ice-cooled distilled water (1,000 ml), while the mixture was continuously stirred by a homogenizer. The desired volume of bio-oil was added so as to give the water-to-oil ratios of 5 : 1, 10 : 1, 15 : 1 and 20 : 1 by volume. The stirring continued after the bio-oil dropping finished. The mixture separated into water-soluble and water-insoluble fractions (WSF and WIF, or pyrolytic lignin). The fractions were separated and filtered to remove the water-soluble fraction and water. The wet water-insoluble fraction (wet WIF) was left. Distilled water was then added to the wet WIF and the mixture was stirred for four hours at room temperature and subsequently dried in a rotary evaporator at 30 °C. The resulting dry pyrolytic lignin was then analyzed. Similarly, the water-soluble fraction was dried at 40 °C. The second fractionation scheme, shown in Fig. 1 as Method B, was a shortened version of the first scheme, without the second round of water addition. Duplicate or triplicate tests were performed and the average is reported here.

3. Bio-oil Characterization

The density was measured by a density meter at 15 °C (DMA 4500 Anton Paar, ASTM D4052). The water content was determined by Karl Fischer titration (809 Titrando, Metrohm Siam Ltd., ASTM

D1744), using Hydranol-Composite 5 and methanol (>=99.9% purity) as a reagent and solvent, respectively. The acidity was measured by potentiometric titration (809 Titrando, Metrohm Siam Ltd., ASTM D664); the sample was dissolved in 100 ml of titration solvent, which was prepared by mixing 500 ml of Toluene (>=99.5% purity), 495 ml of Iso-propanol (>=99.7% purity), and 5 ml of distilled water, and titrated with 0.1 normal of KOH. The dynamic viscosity was determined with a rotational spindle in 8 ml of sample at 40 °C using a viscometer (Brookfield Viscometer Programmable DV-II+, ASTM D445). The heating value was determined by a Bomb Calorimeter (AC-350, LECO Instruments (Thailand) Ltd., ASTM D240). Elemental composition for carbon, hydrogen, and nitrogen was investigated by a CHN analyzer (LECO Instruments (Thailand) Ltd.). The oxygen content was calculated by the difference, assuming that the bio-oil contained only carbon, hydrogen, nitrogen, and oxygen.

The chemical compositions of the starting bio-oil, water-soluble fraction, and pyrolytic lignin were analyzed by gas chromatography/ mass spectrometry (GC/MS). 5 wt% of the sample was diluted in acetone and filtered through a nylon filter with 0.2-μm pore size. Then, 1 L of the sample was injected into the GC/MS system (Shimadzu QP2010 Plus GC/MS). The GC system was equipped with a DB-1701 capillary column as the main column, and a fused-silica capillary column (5 m×0.25 mm ID) as a guard column, which was placed before the main column. The DB-1701 capillary column was 60 m long with 0.25 mm ID, containing 14%-cyanopropyl-phenyl-86%-dimethylpolysiloxane as a stationary phase of 0.25 m film thickness. The injector temperature was set at 280 °C with a split ratio of 1 : 25. The GC oven initial temperature was 45 °C and was held for four minutes. A heating program with heating rates of 4 °C per minute from 45 °C to 240 °C and 6 °C per minute from 240 °C to

270 °C was applied. The final temperature of 270 °C was held for 15 minutes, making the duration of the overall testing program a total of 79 minutes. Helium was the carrier gas, with a velocity of 38 cm/s. The mass spectrometer ion source temperature was 280 °C. The mass range m/z from 35 to 400 was scanned. Data acquisition and processing was performed through GCMS solution, workstation software for GCMS-QP2010 series. The compounds were identified by comparing the mass spectrum (m/z distribution) with the Wiley 7.0 library.
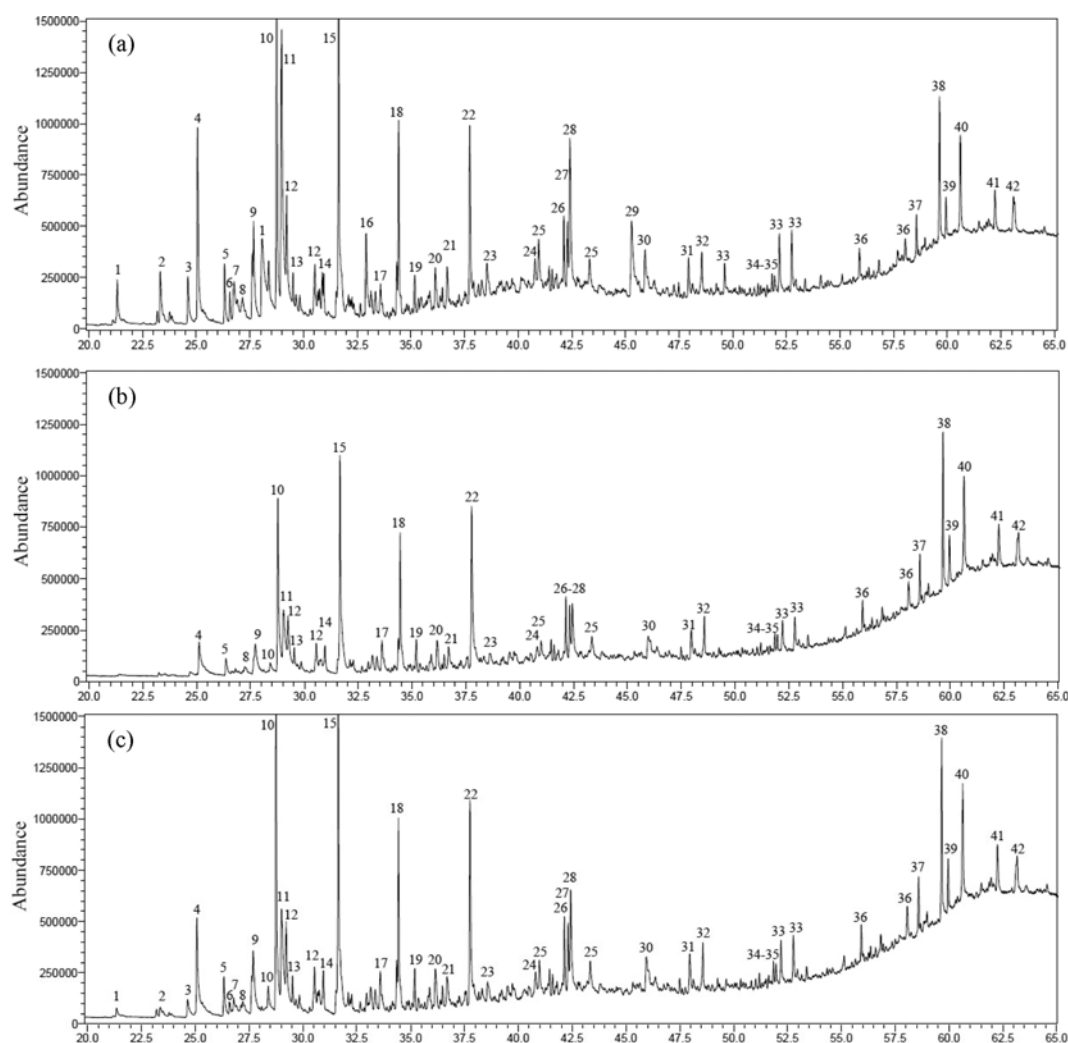
RESULTS AND DISCUSSION

1. Effects of Water-extraction Schemes

Two water-extraction schemes (Method A and Method B) were investigated, as described in the experimental section. Method A was different from Method B in that it had one additional water-extraction step to ensure that all remaining unwanted polar compounds were separated from the pyrolytic lignin. Phase separation took place, as it usually does when the amount of water added di-

Table 1. Properties of the starting bio-oil and pyrolytic lignin, or water-insoluble fractions (WIF), from method a and method B

Properties	Bio-oil[a]	WIF (method A)	WIF (method B)	
		4 °C water	4 °C water	30 °C water
Yield (wt%)	-	35.6	49.0	48.0
Acidity (mg KOH/g oil)	81.3	3.2	27.2	25.4
Viscosity at 40 °C (cP)	114.5	869.0	538.9	499.0
Oxygen content (wt%)	27.2	21.0	23.0	23.0
Heating value (MJ/kg)	25.8	31.4	30.5	30.6
Density at 15 °C (g/cm³)	1.18	1.15	1.16	1.16

[a]As-received properties

Fig. 2. Chromatograms of (a) starting bio-oil, (b) WIF from method A and (c) WIF from method B.

rectly to pyrolysis oil exceeds its maximum water content, which is typically about 30-45 wt% [11]. The aqueous phase on top (the water-soluble fraction) was rich in polar carbohydrate-derived compounds, while the viscous phase at the bottom (pyrolytic lignin) was dominated by less polar lignin-derived chemicals [3]. Table 1 shows that both washing methods improved the properties of the pyrolytic lignin by removing the light compounds, leading to lower acidity,

lower oxygen content, higher carbon content, and higher heating value than those in the starting bio-oil. Method B produced a higher yield of pyrolytic lignin (49.0 wt%) than did Method A. This indicated that the additional water extraction in Method A effectively dissolved more light, polar compounds in the bio-oil into the aqueous, water-soluble fraction. This result was confirmed by the chromatograms of starting bio-oil and pyrolytic lignin extracted from

Table 2. Chemical compositions of the starting bio-oil and pyrolytic lignin, or water-insoluble fractions (WIF), from Method A and Method B

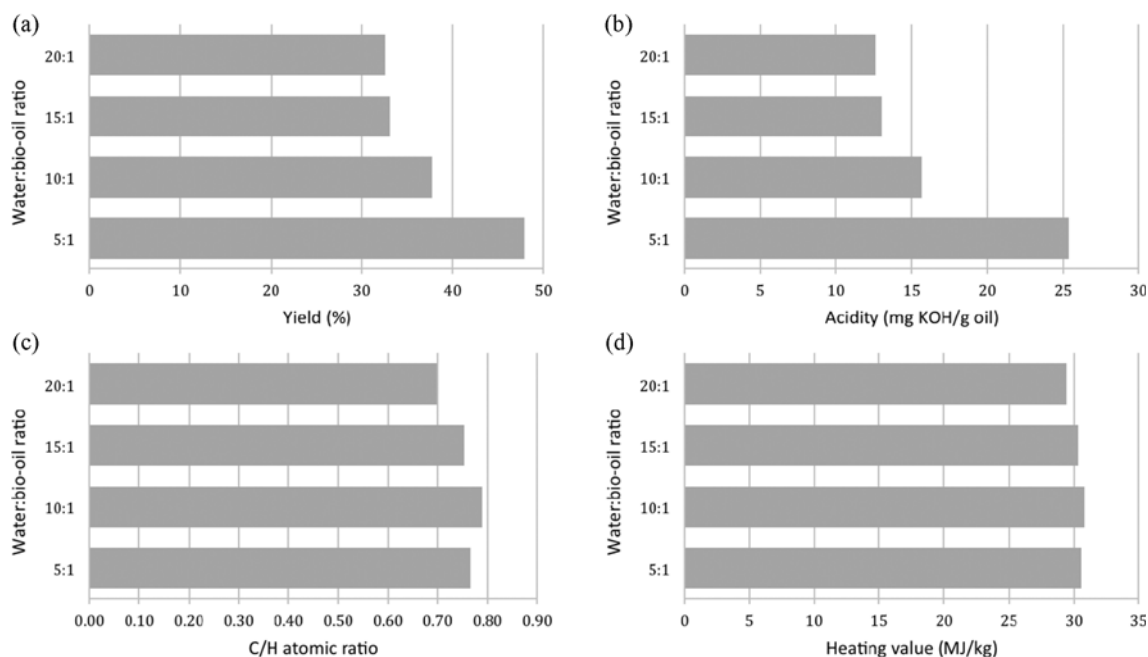| Peak number	Retention time (min)	Compounds name	Bio-oil	WIF	
				Method A	Method B
1	21.31, 28.06	2-Furanmethanol, tetrahydro- [tetrahydrofurfuryl alcohol]	0.88	-	0.51
2	23.31	2-Cyclopenten-1-one, 2-hydroxy-3-methyl- [corylon]	1.51	-	0.65
3	24.60	Phenol	1.18	-	1.16
4	25.05	Phenol, 2-methoxy- [guaiacol]	5.10	4.23	2.09
5	26.31	Phenol, 2-methyl- [o-cresol]	1.39	1.51	0.91
6	26.61	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.65	-	0.38
7	26.75	4H-Pyran-4-one, 3-hydroxy-2-methyl- [maltol]	1.17	-	0.61
8	27.26	2H-Pyran-2-one, tetrahydro-	0.60	0.41	0.79
9	27.67	Phenol, 3-methyl- [m-cresol]	2.81	2.84	1.94
10	28.37, 28.74	2-Methoxy-4-methylphenol	11.93	13.45	10.05
11	28.97	Cyclopropyl carbinol	10.75	7.04	6.05
12	29.20, 30.52	Phenol, 2,3-dimethyl- [o-xylenol]	4.47	5.50	5.62
13	29.50	3,4-Dimethoxytoluene	0.53	0.72	0.93
14	30.94	Benzene, 1,4-dimethoxy-2-methyl-	0.79	0.81	0.78
15	31.63	Phenol, 4-ethyl-2-methoxy- [p-ethylguaiacol]	9.86	11.49	13.17
16	32.91	1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	2.09	-	-
17	33.59	Benzene, 4-ethyl-1,2-dimethoxy-	0.62	1.11	1.47
18	34.42	Phenol, 2-methoxy-4-propyl-	4.42	1.42	6.60
19	35.18	Naphthalene, 1,2,4a,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-	1.04	1.51	1.37
20	36.13	Phenol, 2-methoxy-5-(1-propenyl)-, (E)-	1.35	1.94	1.91
21	36.69	1S,cis-Calamenene	1.09	1.25	0.87
22	37.74	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	4.77	7.71	9.10
23	38.58	Benzaldehyde, 4-hydroxy-3-methoxy- [vanillin]	1.07	0.41	0.73
24	40.78	Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester [vanillic acid]	0.69	0.57	0.67
25	40.95, 43.32	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)- [acetovanillone]	1.85	1.88	1.73
26	42.13	4-Isopropyl-1,6-dimethyl-1,2,3,4,4a,7,8,8a-octahydro-1-naphthalenol	1.36	7.04	0.51
27	42.30	Naphthalene, 1,6-dimethyl-4-(1-methylethyl)- [cadalin]	1.44	2.14	2.30
28	42.41	Propan-2-one, 1-(4-isopropoxy-3-methoxyphenyl)-	4.65	4.48	3.03
29	45.29	D-Allose	3.06	-	-
30	45.91	Benzeneacetic acid, 4-hydroxy-3-methoxy- [homovanillic acid]	1.15	1.06	1.46
31	47.94	Phenol, 2-methoxy-5-(2-propenyl)-	1.07	1.48	1.33
32	48.56	Kaur-15-ene, (5.alpha.,9.alpha.,10.beta.)- [isophyllocladene]	0.59	1.05	1.58
33	49.62, 52.18, 52.75	Furan, 2-butyltetrahydro- [octane, 1,4-epoxy-]	3.48	-	-
34	51.84	Oleic acid, methyl ester	0.23	0.62	0.66
35	51.97	Linoleic acid, methyl ester	0.22	0.49	0.58
36	55.91	Cembrene	0.60	0.98	1.24
37	58.57	Dehydroabietic acid	0.79	1.49	1.78
38	59.64	Ferruginol	3.16	5.31	5.81
39	59.94	Podocarpa-6,8,11,13-tetraen-12-ol, 13-isopropyl-, acetate	0.85	1.58	1.90
40	60.61	Phenol, 2-methoxy-4-(2-propenyl)- [eugenol]	2.26	3.82	4.38
41	62.22	Phenol, 5-[2-(3-hydroxy-5-methoxyphenyl)ethyl]-2-methoxy- [gigantol]	1.07	1.80	2.12
42	63.09	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	1.41	0.85	1.25

Fig. 3. Properties of WIF from Method B with various water : bio-oil ratios (extraction conditions: Method B, room-temperature water, and stirring duration of 2 hours).

both methods, shown in Fig. 2 and Table 2. Most light-compound peaks, especially peaks 1-10, disappeared or weakened. The reduction of peak intensity was more significant in Method A. However, heavy compounds still remained in the pyrolytic lignin (WIF) from both methods. The bigger loss of light-phase compounds in Method A caused a higher increase in viscosity of the WIF. However, the density, oxygen content, and heating value of the extracted pyrolytic lignin from both methods were not much different.

In terms of the operating time, Method B required much less time than did Method A. Thus, it is worth considering choosing Method B over Method A. The only significant difference between the two methods was the acidity of the extracted pyrolytic lignin. The acidity obtained from Method B was still much lower than that of the starting bio-oil. Thus, Method B was selected to further study the effects of washing conditions. Moreover, the results also indicated that water extraction was an effective method for improving bio-oil's quality, especially the acid value and oxygen content.

2. Effects of Water-extraction Operating Conditions

The water temperature was one factor that could affect the properties of pyrolytic lignin. In this study, both cold (4 °C) water, following the method of Scholze and Meier [10], and room-temperature distilled water was used as extraction media. Table 1 shows the properties of pyrolytic lignin extracted with different water temperatures. For this part of the study, the water : bio-oil ratio was set at 5 : 1 by volume and the stirring time was fixed at 2 h. The results indicated that water temperature did not significantly affect the pyrolytic lignin's properties. Therefore, the room-temperature method, which saves the energy required to produce cold water, should be considered.

Method B was chosen over Method A, due to the time saving; however, the acidity of the pyrolytic lignin from method B was still higher than that from method A. In this part of the study, the amount of water used in Method B was investigated, with the hope that more water could remove more polar compounds, including acids. Water :

bio-oil ratios of 5 : 1, 10 : 1, 15 : 1 and 20 : 1 by volume were studied. The amount of water was fixed, while the bio-oil was varied to limit the total volume of liquid in the extraction system, which used a constant stirring speed.

Fig. 3 shows the properties of pyrolytic lignin (yield, acidity, C/H atomic ratio and heating value) extracted with different water : bio-oil ratios. As shown in Fig. 3(a), higher water : bio-oil ratios resulted in lower yields of pyrolytic lignin, indicating that more polar-compounds in bio-oil dissolved into the aqueous phase. This loss of some light-phase compounds caused a decease in the acidity of the pyrolytic lignin, as shown in Fig. 3. The acidity decreased with the increasing water : bio-oil ratios from 5 : 1 to 15 : 1, then converged around 13 mg KOH/g oil.

Even though the water extraction led to a higher carbon content than that in the starting bio-oil, the different water : bio-oil ratios did not significantly affect the elemental composition, and consequently the heating value, of the extracted pyrolytic lignin. The water : bio-oil ratio of 10 : 1 had a high yield and low acidity and should thus be considered. This ratio was also suggested by Scholze and Meier [10].

Influence of the stirring duration was also investigated. The experiments were done with a water : bio-oil ratio of 10 : 1 and water temperature of 30 °C. Fig. 4 shows the properties of pyrolytic lignin extracted with different stirring durations. The results show that the stirring time did not significantly affect the heating value or C/H atomic ratio of the pyrolytic lignin. However, the acidity decreased with increasing stirring duration from 0.5 to 1 h. After that, the acidity became quite stable, indicating that the dissolving of polar compounds in the water was saturated. Thus, the stirring duration should be at least 1 h, in order to effectively reduce the acidity.

3. Properties of Upgraded Bio-oil

Fig. 5 shows the chromatograms of water-soluble fraction and pyrolytic lignin, which was essentially the "upgraded bio-oil," which
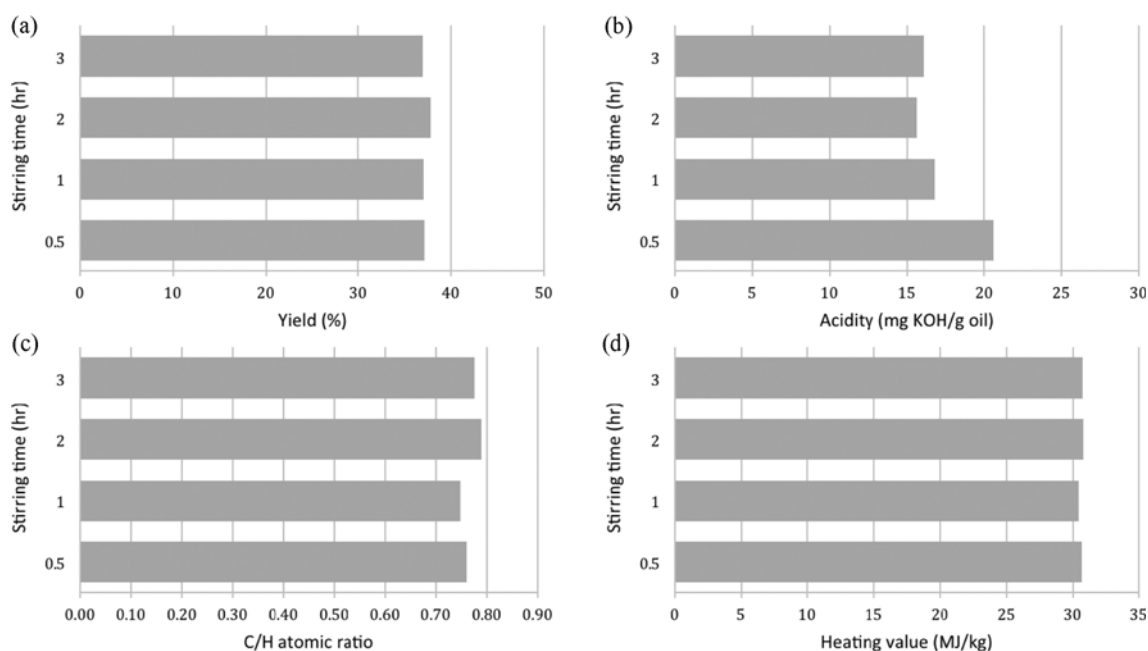
Fig. 4. Properties of WIF from method B with various stirring durations (extraction conditions: method B, water : bio-oil ratio of 10:1, and room-temperature water).
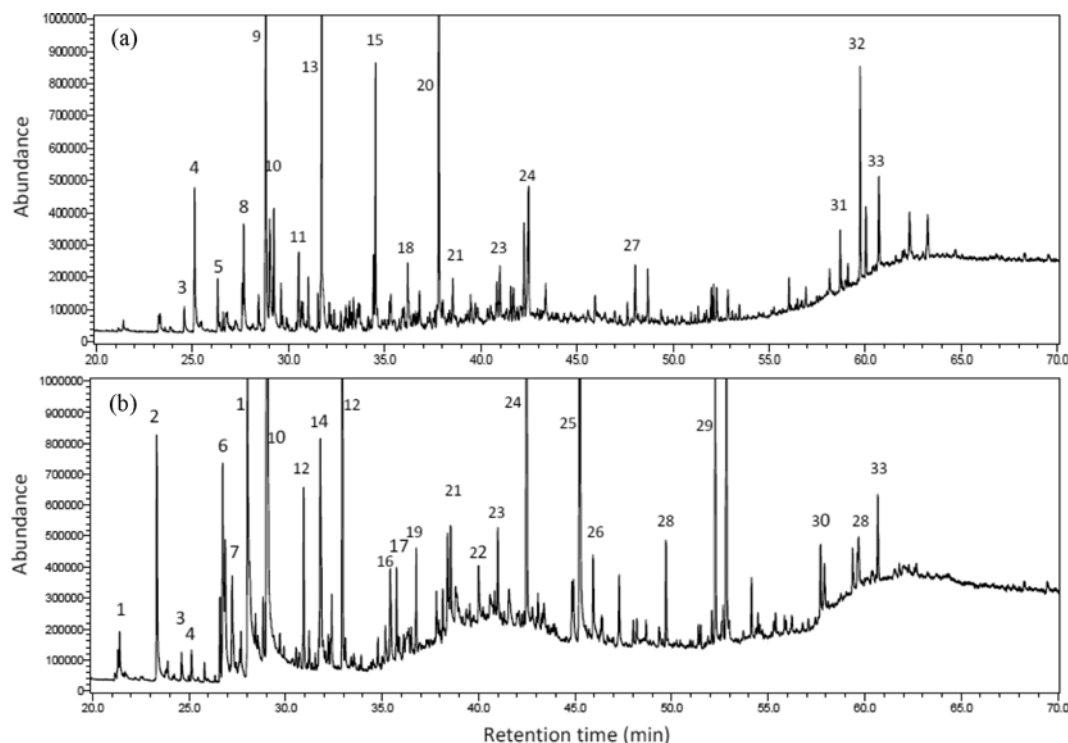

Fig. 5. Chromatograms of (a) WIF and (b) WSF from water extraction with method B, water : bio-oil ratio of 10 : 1, room-temperature water, and stirring duration of 2 hours.

were extracted by Method B with a water : bio-oil ratio of 10 : 1, stirring duration of 2 hours, and at room temperature. More than 50 peaks were found, but only 35 peaks were identified, as listed in Table 3. The peaks can be classified as alcohol, ketone, phenol, carboxylic acid, sugar, phenolic aldehyde, and ether. The water extraction could extract carboxylic acid, sugar, ketone, alcohol, ether, and

some phenol compounds into the water-soluble fraction. Phenols were the main components remaining in the pyrolytic lignin. The removal of some carboxylic acids, such as larixic acid, butanoic acid, 2-propenyl ester, and butanoic acid anhydride, resulted in low acidity in the pyrolytic lignin; however, 1-phenanthrenecarboxylic acid, which had a high boiling point and molecular weight, still re-

Table 3. Chemical compositions of the water-insoluble fraction and pyrolytic lignin, or water-insoluble fractions (WIF)

Peak number	Retention time (min)	Compounds name	WIF	WSF
1	21.42, 28.03	Tetrahydro-2-furanmethanol (Tetrahydrofurfuryl alcohol)	-	0.41
2	23.33	2-Hydroxy-3-methyl- 2-Cyclopenten-1-one (corylon)	-	2.90
3	24.60	Phenol (Izal)	1.25	0.41
4	25.14	2-Methoxy-phenol (guaiacol)	7.41	0.30
5	26.34	2-Methyl-phenol (o-cresol)	1.81	-
6	26.75	Larixic acid	-	2.69
7	27.26	Tetrahydro-2H-pyran-2-one (5-valerolactone)	-	2.05
8	27.63	4-Methyl-phenol (p-cresol)	4.55	-
9	28.85	2-Methoxy-4-methylphenol	18.63	0.85
10	29.05	Cyclopropyl carbinol	5.37	35.31
11	30.56	2,5-Dimethyl-phenol (2,5-xylenol)	3.63	-
12	30.94, 32.95	1,4:3,6-Dianhydro-alpha-d-glucopyranose	-	8.76
13	31.73	4-Ethyl-2-methoxy-phenol	16.08	-
14	31.80	1-Octanol	-	4.48
15	34.55	2-Methoxy-4-propyl-phenol	9.22	-
16	35.42	(S)-(+)-2',3'-Dideoxyribonolactone	-	1.68
17	35.75	2-Furanmethanol, tetrahydro- (tetrahydrofurfuryl alcohol)	-	1.17
18	36.23	2-Methoxy-3-(2-propenyl) phenol	2.32	-
19	36.76	5-Hexen-2-one (allylacetone)	-	1.23
20	37.84	2-Methoxy-4-(1-propenyl) phenol	12.60	-
21	38.58	4-Hydroxy-3-methoxy- benzaldehyde (vanillin)	1.49	1.63
22	40.00	2-Methyl-1,4-Benzenediol	-	0.68
23	41.02	1-(4-Hydroxy-3-methoxyphenyl) ethanone (acetovanillone)	1.94	1.17
24	42.48	2-Methoxy-4-propyl-phenol	5.47	6.25
25	45.21	D-Allose	-	11.66
26	45.96	Methyl-(2-hydoxy-3-ethoxy-benzyl) ether	-	1.65
27	48.06	2-Methoxy-4-(2-propenyl)-phenol (eugenol)	2.44	-
28	49.71, 59.61	Butanoic acid anhydride (butyryl oxide)	-	1.83
29	52.30, 52.83	Tetrahydrofurfuryl acetate	-	10.45
30	57.71, 57.91	2-Butyltetrahydrofuran (Octane, 1,4-epoxy-)	-	1.46
31	58.73	1-Phenanthrenecarboxylic acid	0.98	-
32	59.76	Ferruginol	2.16	-
33	60.74	2-Methoxy-4-(2-propenyl)-phenol (eugenol)	2.64	0.99
34	63.32	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	-	-
35	68.34	Triphenyl-phosphine oxide (triphenylphosphine oxide)	-	-

mained, resulting in the slight acidity of the pyrolytic lignin.

The 1,2-benzenedicarboxylic acid, mono(2-ethylhexyl) ester (peak No. 42 in Fig. 2), which was in the starting bio-oil but not present in the pyrolytic lignin or water-soluble fraction, was likely removed during the drying process. Low-molecular-weight compounds were produced during the degradation of polysaccharides (2-hydroxy-3-methyl-2-Cyclopenten-1-one (Corylon) and decomposition of lignin (4-hydroxy-3-methoxy-benzaldehyde (Vanillin) and 2-methyl-1,4-benzenediol). Some phenol compounds appeared in the water-soluble fraction chromatogram, indicating that it could dissolve in water during the prolonged stirring period [1]. The removal of low-molecular-weight compounds, such as alcohol, ketone, carboxylic acid, and phenolic aldehyde led to the reduction of oxygen atoms, especially the reduction of C=O in pyrolytic lignin. This led to reduced oxidization of the pyrolytic lignin and made it more stable than the starting bio-oil. The acidity of the pyrolytic lignin was also

reduced to 15.6 mg KOH/g oil. Moreover, the removal of low-molecular-weight compounds resulted in the higher viscosity of the pyrolytic lignin (833.3 cP at 40 °C). The pyrolytic lignin had an oxygen content of 21.8 wt%, heating value of 30.8 MJ/kg, and water content of 0.84 wt%. Thus, with a higher heating value, lower acidity, and higher stability, the pyrolytic lignin, or upgraded bio-oil, was significantly better than the starting bio-oil.

CONCLUSION

Water extraction was effective for improving bio-oil properties. The two-step extraction scheme resulted in a lower yield and lower acidity than the one-step scheme, but otherwise the properties of the pyrolytic lignin from both schemes were similar. The stirring time and water temperature did not significantly affect the pyrolytic lignin's properties. The water : bio-oil ratio, however, markedly re-

duced the pyrolytic lignin's acidity. Finally, the resulting pyrolytic lignin had a notably higher heating value, lower acidity, higher stability, and hence higher quality, than the starting bio-oil.

REFERENCES

1. T. Ba, A. Chaala, M. Garcia-Perez, D. Rodrigue and C. Roy, *Energy Fuel*, **18**, 704 (2004).
2. L. Moens, S. K. Black, M. D. Myers and S. Czernik, *Energy Fuel*, **23**, 2695 (2009).
3. D. Mohan, C. U. Pittman and P. H. Steele, *Energy Fuel*, **20**, 848 (2006).
4. L. F. Zilnik and A. Jazbinsek, *Sep. Purif. Technol.*, **86**, 157 (2011).
5. R. Lu, G. P. Sheng, Y. Y. Hu, P. Zheng, H. Jiang, Y. Tang and H. Q. Yu, *Biomass Bioenergy*, **35**, 671 (2001).
6. C. R. Vitasari, G. W. Meindersma and A. B. de Haan, *Bioresour. Technol.*, **102**, 7204 (2011).
7. S. Wang, Y. Gu, Q. Liu, Y. Yao, Z. Guo, Z. Luo and K. Cen, *Fuel Process. Technol.*, **90**, 738 (2009).
8. W. M. Xiong, Y. Fu, F. X. Zeng and Q. X. Guo, *Fuel Process. Technol.*, **92**, 1599 (2011).
9. J. Xu, J. Jiang, W. Lv, W. Dai and Y. Sun, *Biomass Bioenergy*, **34**, 1059 (2010).
10. B. Scholze and D. Meier, *J. Anal. Appl. Pyrol.*, **60**, 41 (2001).
11. R. H. Venderbosch and W. Prins, *Biofuels Bioprod Bioref.*, **4**, 178 (2010).