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Effective Phase Separation of Biomass Pyrolysis Oils by Adding Aqueous Salt Solutions

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Effective separation methods must be developed to generate fractions of similar polarity and to concentrate the undistillable compounds before bio-oils are to be a source of chemicals production. Phase separation is one effective pathway to realize initial separation of bio-oil. By adding a little salt (3 wt % of bio-oil) or aqueous salt solution (10 wt % of bio-oil) including LiCl, $CaCl_2$, $FeCl_3$, $(NH_4)SO_4$, K_2CO_3, and $Fe(NO_3)_3$, the pyrolysis bio-oil of rice husk would quickly form two phases (40−80 wt % of the upper phase, 20−60 wt % of the bottom phase). On the basis of elemental analysis, ^{13}C NMR integrations and GC/MS analysis, it has been demonstrated that some major components in the bio-oil are concentrated in upper/bottom phases respectively. The upper layers exhibit high contents of water, acetic acid, and water-soluble compounds; low density, viscosity, and calorific values; and high distillable substances (up to 65%). The bottom layer consists of low water content, high lignin-pyrolysis compounds, and low distillable substances (<10%), with high viscosity and calorific values. The physiochemical properties of two phases from the phase separation depend on the nature and dosage of salt added.

1. Introduction

Environmental problems and the need to develop value-added chemical products from biomass have in the past 20 years promoted the development of technologies to utilize biomass more efficiently. Many efforts have been made to convert biomass to liquid fuels and chemicals since the oil crises in the mid-1970s.[1,2] Fast-pyrolysis-derived bio-oils have potential as feed stocks for chemical production[3−8] and as a promising route to liquid fuels.[1,8−11] The composition and properties of the oils differ considerably from those of petroleum-based fuel oils. Because of some special properties of pyrolysis oils, many problems arise in their handing and utilization.[1,12]

Biomass-based pyrolysis oils have complex chemical composition, including a large amount of water, carboxylic acids, carbolydrates, and lignin-derived substances. The oils are acidic, viscous, reactive, and thermally unstable.[1] The prevalence of dimeric to tetragmeric phenolic lignin decomposition products in bio-oil, together with water and a plethora of compounds of many classes, makes the fractional distillation of bio-oil impossible. Because of the huge range of polarities and the large fraction of oxygenated compounds, it is very difficult to separate the oils by column chromatography. Therefore, before bio-oils are to be a source of chemicals production, effective separation methods must be developed to generate fractions of similar polarity and to concentrate the undistillable compounds.[1]

The morphology and the chemical composition of bio-oils are strongly dependent on the pyrolysis process and the nature of the feedstock used. A microscopic analysis of bio-oils reveals the presence of a multiphase system that has been formed by solid particles, pasty structures, and droplets that constitute a complex colloidal system.[13] Bio-oils can be separated into water-soluble materials (high-polarity compounds) and water-insoluble materials (low-polarity components). The water-insoluble materials are called lignin-derivative compounds, or pyrolytic lignin.[7,14] Depending on the dissolving strength of the continuous medium, which consists of water-soluble compounds, the lignin-derivative molecules can be found in a molecular state or in an associate form. It has been shown by previous researchers that in the presence of a large amount of water, the lignin derivative molecules spontaneously precipitate.[15]

Addition of water into pyrolysis oil in a sufficient amount results in a phase separation. Upon adding water, a viscous oligomeric lignin-containing fraction settles at the bottom, whereas a water-soluble fraction rich in carbohydrate-derived compounds form an upper layer. Effective phase separation is beneficial to separate and utilize the two phases. However, much

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overlap of compound types exist in both fractions, and addition of large water quantities would result in further difficulty of separation.

Osamaa et al. reported that fast pyrolysis of forestry residue produced an extractive-rich upper phase that varies from 10 to 25% of the total product and a bottom phase closely resembling the normal bark-free wood product. Phase separation occurs due to the higher extractive content of the residues which, due to their much lower oxygen content. Extractives are composed of hydrophobic components with a low polarity and density and phase separate, forming an upper phase that has a higher viscosity and heating value than the bottom phase.[16−18]

In this work, through adding inorganic salts in 3 wt % of bio-oil or their solutions in 10 wt % of a bio-oil, the bio-oil can form two phases, upper/bottom layers, thus the bio-oil would be separated into two fractions. Some major components in bio-oil were concentrated in upper/bottom phase, respectively. This phase-separation process is similar with the sailing out of proteins. This separation method would have a potential as an initial separation of bio-oils.

2. Experimental Section

2.1. Bio-oil Production. The bio-oil studied herein has been obtained via fast pyrolysis of rice husk in an autothermal fluidized-bed pyrolyzer with a capacity of 120 kg/h oil at our laboratory (Anhui Province Key Laboratory for Biomass Clean Energy, University of Science and Technology of China). The pyrolysis device mainly consists of a hopper, two screw feeders, an electric heater, a fluidized-bed reactor, two cyclones, a condenser, and an oil pump, as well as some thermocouples and pressure meters. The hopper is used to contain feedstock such as rice husks, sawdust, or their mixture. The two screw feeders have the same configuration and size; the first one is used to control the feeding rate and the second one operates at a relatively high speed to prevent jamming of the feeding system. The fluidized-bed reactor has a height of 2 m and a diameter of 0.7 m, in which rice husks or sawdust are rapidly heated for pyrolysis. The electric heater can preheat the nitrogen to the temperature range of 450−550 °C before entering into the fluidized-bed reactor. The two cyclones are used to separate solid particles such as charcoal and ash from the hot gas. The condenser is equipped with some nozzles and a heat exchanger. The condenser can quickly cool the cleaned hot gas into a liquid. An oil pump is used to pump the condensed liquid from the bottom of the condenser to the nozzles on the top of the condenser. Pumping the cooled liquid back into the condenser assists in the scrubbing and condensation process. Thermocouples and pressure meters are used to monitor and control the pyrolysis system. More characteristics of the pyrolysis reactor have been described elsewhere.[19] Physiochemical properties of the whole bio-oils used in this work are listed in Table 1.

2.2. Phase Separation of Bio-oil. Phase separations of the bio-oil were performed through adding various inorganic salts into bio-oils. Samples of the bio-oil (10 mL) were placeed into glass tubes (15 mm in diameter, with a capacity of 15 mL) and 0.3 g salt or 1 mL of 30% salt aqueous solution were added with stirring and sonication in a water-cooled bath below 15 °C. Afterward, the tubes were sealed with parafilm and stored for 10 h at room temperature, forming two phases (upper/ bottom layer). The upper layer was removed through pouring out from the tube for a large difference in viscosity of two phases, and the two phases were weighted and characterized, respectively.

Table 1. Physiochemical Properties of the Whole Oils in This Work

property	bio-oil A	bio-oil B
water content	26.7 wt %	32.5 wt %
density	1.15 kg/L	1.19 kg/L
viscoisity at 40 °C	25.6 cSt	12.1 cSt
heating value, MJ/kg	16.9	16.5
pH	3.2	2.8
element composition, wt %		
C	37.9	36.3
H	7.39	7.35
N	0.74	0.48
O (by difference)	53.9	55.8

2.3. Physicochemical Characterization. Physicochemical properties, such as density, pH value, water content, gross calorific value, and viscosity were determined using standard ASTM methods. The elemental composition (carbon, hydrogen, and nitrogen) was determined in an Elementar Vario El-III analyzer. The oxygen content was calculated by difference.

2.4. Nuclear Magnetic Resonance Analysis. ^{13}C NMR spectra of whole bio-oil and of the two phases were recorded in DMSO-d_6 solutions at 100.6 MHz using a Bruker 400 MHz spectrometer according to the method in a literature.[20] Solutions of 30 wt % samples were employed. About 10^4 scans were accumulated for each sample ^{13}C spectrum using a 90° pluse width together with broadband proton decoupling. Tubes of 5 mm diameter were used. Inverse gated decoupling was applied to void NOE effects in the ^{13}C spectra. The integrated ^{13}C spectra were divided into five general chemical shift ranges for analysis: 215−163 ppm (carbonyl carbons), 163−110 ppm (total aromatic carbons), 110−84 ppm (carbohydrate-type carbons), 84−54 ppm (methoxy- or hydroxy-bound carbons), and 54−1 ppm (primary, secondary, tertiary, and most quaternary alkyl carbons). The aromatic region was further subdivided into 125−112 ppm (guaiacyl carbons) and 112−110 ppm (syringyl carbons).[20]

2.5. Solvent Fractionation of the Upper Layer and the Bottom Layer and Gas Chromatography /Mass Spectrometry (GC/MS) Analysis. ~10 mL of the upper layer from phase separation was extracted three times (3 × 50 mL) with diethylether. The ether-insoluble fraction was removed by filtraction. The filtrate was dried with anhydrous Na_2SO_4 and filtered. The ether-solubles and ether-insolubles were evaporated (<30 °C), and the dried residues were weighed. Similarly, ~2 g of the bottom layer was extracted with dichloromethane (DCM) for three times (3 × 50 mL). The DCM-insoluble fraction was removed by filtraction. The filtrate was dried with anhydrous Na_2SO_4 and filtered. The DCM-solubles and DCM-insolubles were evaporated (<40 °C), and the dried residues were weighed.

The whole bio-oil and the fraction recovered of the upper layer and the bottom layer were dissolved in methanol, and dried with anhydrous Na_2SO_4 and filtered. The filtrates were analyzed by GC/MS (using an Varian 24cb fused silica capillary column, 30 m × 0.25 mm i.d., film thickness 0.25 μm), and the compounds of various fractions were identified by GC/MS. Helium was used as the carrier gas, and the gas flow was held constant at 1 mL/min. The injector temperature was 280 °C. The temperature program was 2 min at 40 °C, then at 4 °C /min to 280 °C, and 5 min at 280 °C. The interpretation of the spectra obtained by GC/MS spectrometry was based on automatic library search and literature

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Table 2. Mass Percentages, Water Contents, Heating Values (HV), and Elemental Analysis for Two Phases from Phase Separation of Bio-oil A[a]

sample		mass wt %	H_2O (wt %)	HV (MJ/kg)	elemental analysis (wt %) C	H	N	O[b]	C/H
bio-oil A			26.7	16.9	37.9	7.39	0.74	54	5.1
LiCl	U[c]	52	47.8	10.8	26.8	7.67	0.27	65	3.5
	B[c]	48	5.8	22.0	50.3	7.13	1.23	41	7.1
$FeCl_3$	U	49	40.2	12.3	27.1	7.81	0.52	65	3.5
	B	51	10.5	19.8	46.7	7.07	1.21	45	6.0
$(NH_4)_2SO_4$	U	38	48.5	11.2	30.5	8.42	2.19	59	3.6
	B	62	10.7	20.1	42.7	7.83	1.32	48	6.0
$Fe(NO_3)_3$[d]	U	61	35.7	13.2	33.1	7.06	1.42	59	4.2
	B	39	13.2	19.1	48.8	7.34	1.81	42	6.7

[a] Salts added in 3 wt % of the bio-oil, unless otherwise indicated. [b] Calculated by difference. [c] U: upper layer, B: bottom layer. [d] In 4 wt % of the bio-oil.

Table 3. Average Values for Mass Ratio, Water Contents, Calorific Values for Two Phases from Phase Separation of Bio-oil B[a]

reagents added	M[b]	mass ratio U:B[c]	density U	density B	H_2O (wt %) U	H_2O (wt %) B	HV (MJ/kg) U	HV (MJ/kg) B
H_2O		95: 5	1.15	1.22	39.7	18.6	12.8	23.0
LiCl[d]	2.36	64:36	1.18	1.25	41.8	16.3	11.2	28.0
LiCl	0.64	74:26	1.14	1.21	42.6	16.5	12.6	23.4
$CaCl_2$	0.24	74:26	1.13	1.23	42.0	17.8	12.4	23.8
$(NH_4)_2SO_4$	0.21	78:22	1.16	1.23	40.1	19.0	12.5	23.3
K_2CO_3	0.20	74:26	1.14	1.27	42.4	17.3	13.7	24.5

[a] 30% aqueous solution in 10 wt % of the bio-oil, unless otherwise indicated. [b] Molar concentrations of salt in bio-oil. [c] U: upper layer, B: bottom layer. [d] Neat LiCl in 10 wt % of the bio-oil.

data.[21−24] Peak area obtained from the ion chromatography is a qualitative content of a compound.

3. Results and Discussion

3.1. Salt-induced Phase Separation of Bio-oil. Addition of a little salt results in phase separation, and ratios of two phases are ca. 50:50 for LiCl and $FeCl_3$, 38:62 for $(NH_4)_2SO_4$, and 61:39 for $Fe(NO_3)_3$. The water content of the upper lighter layer is 3−9 times more than that of the bottom layer, and the heating value of the bottom heavy fraction is about twice the upper lighter layer (Table 2).

Several solutions of inorganic salts (30 wt %) were added to bio-oil B, and phase separation occurred to form two phases after storage for 10 h at room temperature. Because of a large difference in viscosities between upper and bottom phases (4.8 cSt for upper phase, 334.2 cSt for bottom phase for LiCl solution-treating bio-oil), the upper phases can be poured out, and two phases were weighted respectively. The mass ratio of two phases and densities are listed in Table 3.

After addition of water in 10 wt % of the bio-oil, the phase separation also occurs, and the boundary line of two phases is obscure, and the mass of the bottom layer is also less. Adding LiCl salt in 10% of bio-oil, the proportion of bottom layer is higher than that of its aqueous solution. Experiments further show that proportions of the bottom layers increase with mass and concentration of salt solution added. Adding 30 wt % salt solution in 10 wt % of bio-oil, the ratios of two phases are similar for all four salt solutions. If the percent concentration (30 wt %) is changed as a molar concentration, the molar concentration of LiCl solution is about three times of other three solutions. For the product of ion number and charge in a solution, the latter three solutions are about three times that of the LiCl solution. Thus, the phase separation depends on the number of ions and the charge of ions in a salt solution added.

Table 4. Elemental Composition of the Whole Bio-oil B and Corresponding Phase-separating Bio-oils[a]

sample	solutions added	elemental analysis (wt %) C	H	N	O[b]	C/H
bio-oil		36.3	7.35	0.48	56	4.9
upper layer	LiCl	29.2	7.92	0.29	63	3.7
	$CaCl_2$	28.9	7.94	0.28	63	3.6
	$(NH_4)_2SO_4$	28.6	8.04	0.86	63	3.6
	K_2CO_3	30.8	7.88	0.33	61	3.9
bottom layer	LiCl	51.4	6.80	0.64	41	7.6
	$CaCl_2$	51.6	6.81	0.79	41	7.6
	$(NH_4)_2SO_4$	51.3	6.82	0.90	41	7.5
	K_2CO_3	52.0	6.82	0.65	41	7.6

[a] 30% aqueous solution in 10 wt % of the bio-oil. [b] Calculated by difference.

Table 5. ^{13}C NMR Integrations (%) for Whole Bio-oil B and Corresponding Separating Bio-oils

type of carbon	δ (ppm)	bio-oil B (%)	LiCl U[a]	LiCl B[a]	K_2CO_3 U	K_2CO_3 B
carbonyl	215−163	17.9	18.3	12.0	17.6	9.3
total aromatic	163−110	19.1	12.8	42.4	16.0	48.7
aromatic (guaiacyl)	125−112	10.7	6.7	18.0	6.9	18.8
aromatic (syringyl)	112−110	0.2	0.2	1.0	0.2	1.8
carbohydrate	110−84	8.8	11.6	3.2	11.3	1.9
mthoxy/hydroxy	84−54	30.5	36.8	17.2	33.8	14.4
alkyl carbons	54−1	23.3	20.6	25.1	21.3	25.6

[a] U: upper layer, B: bottom layer.

3.2. Physicochemical Properties of Two Phases. The water content of the upper lighter layer is usually two or more times higher than that of the bottom phase, and calorific values of upper layers are two times lower than those of bottom phases. These data show that the upper layers include large amount of water and water-soluble compounds with high oxygen contents, such as carbonyl acids, "sugar", and alcohol, etc. Among them, properties for LiCl salt-treating bio-oil are the most different between two phases. For example, the water content of the bottom layer is the lowest, and the largest difference in calorific values of two phases, 11.2 MJ/kg for the upper layer and 28 MJ/kg for the bottom layer.

Elemental Composition of the Two Phases. The elemental composition of two phases and the whole bio-oil were determined and are listed in Tables 2 and 4, respectively. The carbon contents of bottom layers are nearly twice those of upper layers. This is in agreement with the difference in their heating values. Hydrogen content of the upper layer is higher than that of the bottom phase. Both hydrogen content and nitrogen content in the upper layer of $(NH_4)_2SO_4$ sample are higher than the corresponding values of other samples. Carbon content in the upper layer of K_2CO_3 sample is higher than those of other samples. These indicate that salt solutions added are mainly distributed in the upper phases.

NMR Analysis. ^{13}C NMR integrations for the whole bio-oil and treating bio-oils with two salt solutions were determined. The integrate region was divided into seven ranges, listed in Table 5. Data show that carbonyl, carbohydrate, and methoxy/hydroxy carbons are much higher for upper phases over bottom phases, and alkyl carbons in upper phases are less than those in bottom phases. The proportion of various aromatic carbons (total aromatic, guaiacyl, and syringyl carbons) in upper phases is much lower than that in bottom phases. These clearly show that upper phases include more carbonyl, methoxy/hydroxyl compounds, such as carbonyl acids, carbohydrate, aldehyde,

Table 6. Elemental Composition of Solvent Fraction of Two Phases from Phase Separation of Bio-oil B

sample			yield (wt %)	elemental analysis (wt %) C	H	N	O[a]	C/H
upper	ether-so1uble	LiCl	28.4	49.7	6.95	0.31	43.1	7.2
		K_2CO_3	27.4	50.7	6.84	0.31	42.1	7.4
	ether-insoluble	LiCl	57.9	23.3	8.09	0.32	68.3	2.9
		K_2CO_3	56.5	26.7	8.09	0.49	64.7	3.3
bottom	DCM-soluble	LiCl	52.2	58.6	6.09	0.36	35.0	9.6
		K_2CO_3	45.8	58.1	5.98	0.36	35.6	9.7
	DCM-insoluble	LiCl	41.0	56.5	5.82	1.21	36.4	9.7
		K_2CO_3	45.0	56.1	5.62	1.10	37.2	10.0

[a] Calculated by difference.

ketone, and alcohols, and bottom phases are lignin-pyrolysis products with phenyl rings.

Solvent Fractionation of the Upper Layer and the Bottom Layer. The upper-layer bio-oils from phase separation induced by LiCl and K_2CO_3 solutions were dissolved in diethylether. The ether-insoluble fraction was removed by filtration. The ether solubles and insolubles were evaporated (<30 °C) and weighted, the percentage corresponding to each fraction and their elemental compositions are presented in Table 6. The ether solubles have only about 28%, and up to 58% for the ether insolubles in upper phases. In addition, a part of the volatile compounds was lost in evaporation, and these compounds should be low-boiling-point.

In the same way, the bottom-layer bio-oils from phase separation induced by LiCl and K_2CO_3 solutions were dissolved in dichloromethane (DCM). The DCM-insoluble fraction was removed by filtration. The DCM solubles and insolubles were evaporated (<40 °C) and weighted, and the percentage corresponding to each fraction and their elemental compositions are presented in Table 6. The DCM solubles have similar percentages to the DCM insolubles, 40−50%. The percentages of the DCM solubles for LiCl sample are higher than those of K_2CO_3, and the DCM insolubles of K_2CO_3 sample higher over LiCl sample. In evaporation, a part of volatile compounds for bottom layers were also lost, and much less than upper layers. Comparing percentages of solubles in two phases, those in the bottom layers (ca. 52%) are nearly twice more than those in the upper layers (ca. 28%).

The chemical compositions of the upper layer are different from the compositions of the bottom layer and of the whole bio-oil. Bottom layers have higher non- or low-polarity solvent-soluble fractions than upper layers and the whole bio-oil. Contrary to this, bottom layers exhibit the lowest content of high-polarity methanol-soluble fraction, and upper layers have the highest methanol-soluble fraction (near to 100%). These differences are due to high polarity of upper layers, related to low polarity of bottom layers. The fractions recovered were further analyzed by GC/MS, shown in Figure 1.

GC/MS Analysis of the Fractions Obtained. The whole bio-oil and DCM-soluble fractions of the two phases of LiCl-solution treating bio-oil were dissolved in methanol, dried with anhydrous Na_2SO_4, and filtered. The filtrates were analyzed by GC/MS. The chromatograms are shown in Figure 1, and the main compounds identified are listed in Table 7.

Acetic acid in the upper layer has very high proportion, and less for the bottom layer. Some high-polarity compounds have higher proportions in the upper layer over bottom layer, such as ketone (No. 4), alcohols (21, 22), bisphenol (35), etc. Compounds with high proportions in the bottom layer are most lignin-pyrolysis compounds, such as 18, 23, 24, 26, 33, 34, 36, 37, 41−45, 47, 48, 50−52, 54−56, 58, and 59. Total percentages

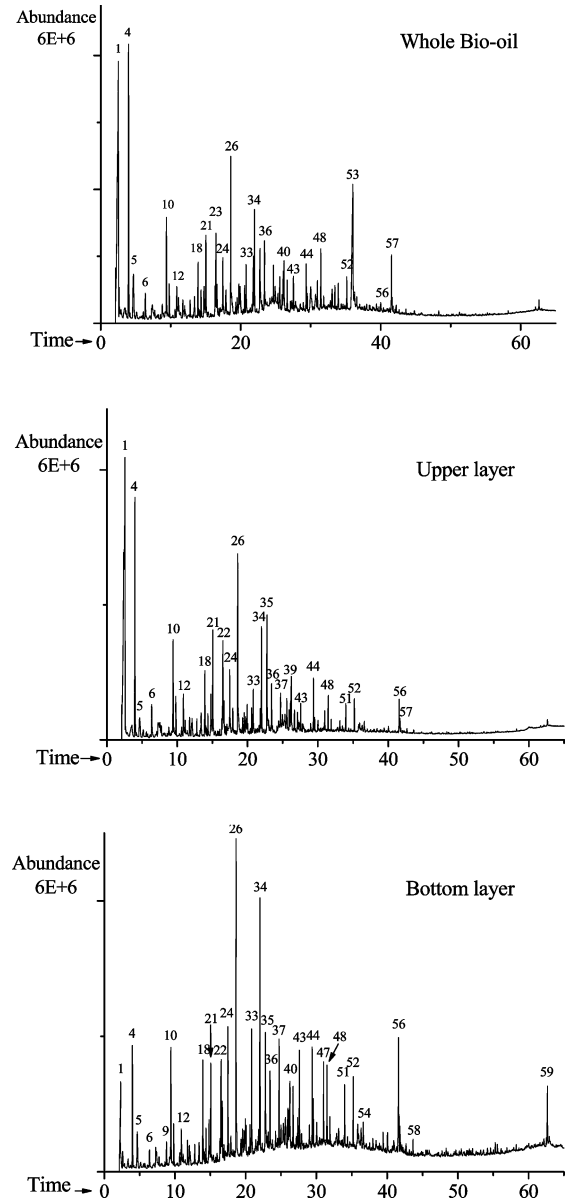

Figure 1. Total ion chromatography for the whole bio-oil B and DCM-soluble fraction of two phases from LiCl solution-induced phase separation.

of lignin-pyrolysis products (or compounds with phenyl groups) are 26.0, 28.6, and 50.4% for whole bio-oil, the upper layer, and the bottom layer, respectively. The extractive contents of two phases show near to twice in the bottom layers over the upper layers'. Thus, the content of pyrolytic lignin in the bottom layers should be 3−4 times more than those in the upper layers. There is one compound with high proportions in the whole bio-oil, levoglucosan (53), but it is very less in the soluble fractions of two phases. This may be that this compound with high polarity cannot be extracted by a low-polarity solvent, dichloromethane. Although it was not detected in the soluble fractions of two phases, it should be distributed in the upper layers with high polarity.

Bio-oils represent a complex colloidal multidispersed system containing char particles, waxy materials (e.g., fatty acids, fatty alconols, sterols, and aliphatic hydrocarbons), and aqueous droplets and micelles formed from lignin derivatives in a matrix of hollocellulose-derivatived compounds and water.[25,26] The

Table 7. Chemical Composition of the Upper Layer, the Bottom Layer, and Whole Bio-oil B

peak No.	main and indentified compounds	RT[a] (min)	mol mass	peak areas (%)		
				bio-oil B	U[b]	B[b]
1	acetic acid	2.31	60	20.1	28.3	3.82
2	hydroxyacetaladehyde	2.61	60	0.48	<0.01	0.34
3	propanoic acid	3.57	147	<0.01	1.18	<0.01
4	acetol	3.96	74	7.89	7.72	2.93
5	glycerin	4.66	43/45/61	2.73	1.31	1.75
6	1-hdroxy-2-butanone	6.38	88	0.72	1.05	0.47
7	ethylene glycol monoacetate	7.27	43/73/86	<0.01	0.45	0.58
8	2, 3-dihydroxypropanal	7.38	90	1.26	0.7	0.63
9	butanedial	8.80	43/57/58	0.5	<0.01	0.61
10	3-furfural	9.41	96	2.59	2.63	3.34
11	2-cyclopenten-1-one	9.81	82	0.91	1.08	1
12	1-acetyloxy-2-propanone	10.89	116	1.02	1.41	1.05
13	2-methyl-2-cyclopenten-1-one	11.77	96	0.6	0.73	0.76
14	1-(2-furanyl)-ethanone	12.03	110	0.33	0.37	0.51
15	unknown	12.13	142	<0.01	0.73	0.44
16	2-hydroxy-2-cyclopenten-1-one	12.79	98	0.43	0.46	0.45
17	3-furan methanol	13.40	98	0.71	0.87	0.66
18	phenol	13.93	94	1.54	1.99	2.76
19	5-methyl-2-furfural	14.38	110	0.7	0.6	0.84
20	3-methyl-2-cyclopenten-1-one	14.80	96	1.24	1.76	1.62
21	2(5*H*)-furanone	15.06	84	2.57	3.67	2.88
22	2-hydroxy-3-methyl-2-cyclopenten-1-one	16.52	112	2.5	3.73	3.56
23	*o*-cresol	16.68	108	0.96	1.22	1.66
24	*m*-cresol	17.49	108	1.92	2.59	2.96
25	unknown	17.90	43/57/73	1.15	1	0.63
26	guaiacol	18.63	124	3.58	4.96	7.9
27	methyl 2-furoate	19.32	126	0.27	0.42	0.39
28	3-ethyl-2-hydroxy-2-cyclopenten-1-one	19.53	126	0.51	0.71	0.98
29	5-hydroxymethyldihydrofuran-2-one	19.75	116	1.48	0.63	0.92
30	4-methyl-5*H*-furan-2-one	19.95	98	0.72	0.7	0.83
31	2,3-xylenol	20.05	122	0.27	<0.01	0.56
32	maltol	20.60	126	0.69	0.62	0.63
33	*p*-ethylphenol	20.82	122	1.37	1.31	3.18
34	4-methylguaiacol	22.01	138	2.4	2.72	5.82
35	catechol	22.78	110	2.36	4.04	3.8
36	coumaran	23.44	120	1.62	1.15	1.82
37	4-ethylguaiacol	24.71	152	0.99	0.97	2.14
38	1.4:3.6-dianhydro-D-glucopyranose	25.57	69/98/99	0.93	1.14	<0.01
39	unknown	26.13	43/60/97	0.92	0.75	0.93
40	5-hydroxymethyl-2-furaldehyde	26.24	126	1.11	1.48	1.58
41	4-vinylguaiacol	26.69	150	0.51	0.48	1.29
42	α-ethyl-*p*-methoxybenzyl alcohol	27.35	166	<0.01	<0.01	0.78
43	eugenol	27.58	164	0.71	0.61	1.87
44	syringol	29.41	154	1.06	1.39	2.12
45	5-propenylguaiacol	29.56	164	0.33	0.33	0.93
46	unknown	30.70	240	1.03	<0.01	<0.01
47	isoeugenol	31.01	164	0.65	0.55	1.88
48	vanillin	31.49	152	1.32	0.86	1.66
49	2-hydroxy-3-isopropyl-6-methyl-2-cyclohexen-1-one	31.91	168	<0.01	0.28	0.55
50	4-propanylguaiacol	33.14	166	<0.01	0.36	0.46
51	4-acetylguaiacol	33.96	166	0.64	0.75	1.47
52	guaiacylacetone	35.18	180	0.8	0.76	1.39
53	levoglucosan	36.02	60/73/98	10.29	<0.01	<0.01
54	coniferyl alcohol	36.62	180	0.32	0.3	0.78
55	4-allylsyringol	39.42	194	<0.01	<0.01	0.45
56	4-hydroxy-2-methoxycinnamaldehyde	41.60	178	1.48	0.94	3.5
57	4-acetylsyringol	41.64	196	0.37	0.37	<0.01
58	4-hydroxy-3-methoxy-cinnamic acid methyl ester	43.66	208	<0.01	<0.01	0.34
59	2,3-dimethoxy-10,11-dihydro-dibenzo[b,f]oxepin-10-ol	62.67	272	<0.01	<0.01	1.75

[a] Retention time. [b] U: upper layer, B: bottom layer.

lignin derivatives are assumed to be solvated in the system by the water-soluble molecules, where they agglomerate and form micelles. On this account, the lignin-derived water-insoluble fraction would be suspended in micellar or microemulsion phases by the continuous aqueous phase, which acts as a bridging agent between the high-molecular-mass lignin and the continuous aqueous phase. Addition of a salt aqueous solution into the bio-oil causes precipitation of the lignin fraction by destroying hydrogen bonds and dispersing the bridging components, which causes agglomerization and separation of the lignin micelles. Meanwhile, water-insoluble compounds with low polarity separate from aqueous phase and agglomerate with the lignin derivatives. In addition, the complex may be formed between pyrolytic lignin and metal ion such as ferrum ion,

(25) Garcia-Perez, M.; Chaala, A.; Pakdel, H.; Kretschmer, D.; Rodrigue, D.; Roy, C. *Energy Fuels* **2006**, *20*, 364–375.

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leading it to settle at the bottom. Therefore, addition of salt aqueous solution breaks the weak equilibrium of the bio-oil system and causes phase separation. This phase-separation is similar to the salting out of proteins to some extent.

4. Conclusion

The major conclusion of this study is that addition of a little salt (3 wt % of bio-oil) or a solution (10 wt % of bio-oil) into bio-oil can quickly result in phase separation (40−80 wt % of top phase, 20−60 wt % of bottom phase), and the ratio of the two phases depends on salt added and its dosage. Some compounds with similar polarity are concentrated in different phases, such as acetic acid, alcohols, and other water-soluble compounds in upper layers, and lignin-pyrolysis compounds in bottom layers. Phase separation forming two phases have large differences in physcochemical properties. The upper layers exhibit high contents of water, acetic acid, and water-soluble compounds, low density and viscosity, low calorific values, and high distillable substances (up to 65%); and the bottom layers have right contrary properties, low contents of water, high lignin-pyrolysis compounds, high viscosity and calorific values, and low distillable substances (<10%). The nature of salt and its dosage would influence the physicochemical properties and components of the two phases from the phase separation. However, addition of neat water in 10 wt % of bio-oil results in a very low proportion of the bottom, 5%, and the two phases do not have large differences in their physcochemical properties. Addition of salt aqueous solution would destroy hydrogen bonds and enhance polarity of aqueous phase, and cause agglomerization and separation of the lignin micells. This phase separation is promising as a method for initial separation of bio-oils.

Further research will be focused on optimizing the phase separation conditions for various salts or salt solutions, and effective utilization of two phases, such as distillization to upper layers and fraction with solvents of bottom layers.

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