Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks

Zhengang Liu ^{a,b}, Fu-Shen Zhang ^{a,*}

^a Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China

^b Graduate University of Chinese Academy of Sciences, Beijing 100039, China

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ABSTRACT

The liquefaction of pinewood in the presence of various solvents (water, acetone and ethanol) was studied so as to investigate the solvent effects on the biomass liquefaction process. Experiments were conducted in an autoclave in the conditions of temperature range 523–723 K, starting pressure 1 MPa, reaction time 20 min, biomass 10 g and solvent 60 g, respectively. The liquid products and solid residues were characterized by GC–MS and FTIR. The results showed that the liquefaction products were greatly affected by the solvent type. With acetone as extraction agent, 4-methyl-1,2-benzenediol was one of the major compounds, while ethanol favored the formation of (*E*)-2-methoxy-4-(1-propenyl)-phenol and water significantly narrowed the products distribution. Among the tested solvents, acetone had the highest conversion rate, while the highest oil yield reached 26.5% at 473 K in ethanol. The FTIR analysis showed that cellulose liquefaction speed in water preceded in acetone and ethanol, and the solid residue consisted of solid carbon and a little amount of lignin fragments at 723 K.

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1. Introduction

Renewable energy is growing important in responding to concerns over the environment pollution and the shortage of energy supplies [1,2]. Biomass is viewed as one of the most important potential and the only carbon-containing renewable energy resources. The term biomass can generally be defined as all the biologically produced matter, mainly in form of abundant agricultural and forestry wastes [3]. In the past decades, biochemical (such as methane and alcoholic fermentation) and thermal-chemical conversion technologies and processes have been studied for the utilization of biomass as feedstock for chemicals and bio-fuels [4–7]. In these methods, thermal liquefaction is considered to be most promising method obtaining low molecular weight liquid, gas fuel and solid residue. Among thermal liquefaction conversion, pyrolysis and solvolysis are two main research focuses on converting biomass to more useful chemicals and fuels. Thus far, nearly 100 different biomasses, such as nutshell, corn stover, cherry stones, pinewood, sawdust, have been employed pyrolysis conditions, [8]. However, the high operating temperature of pyrolysis (673–1273 K) can lead to cross-linking reaction between hydrocarbons and aromatics resulting in tar which is difficult to further decompose. The solvolysis has many advantages such as (1) The presence of solvent dilute the concentration of the products pre-

venting the cross linked reactions and reverse reactions and (2) Relative low temperature (less energy consumption) in comparison with pyrolysis and gasification. Solvent has remarkable effect on the liquefaction reaction, for example, the use of supercritical alcohol, rather than water successes in converting low rank coal into liquid oil [9,10]. Some articles have been reported about the solvolysis liquefaction of biomass and the presences of organic solvents are proven effectively to lower the viscosity of heavy oil derived from biomass liquefaction [11]. Because of the economic and environmental reasons, tested solvents of industrial interests tended to be those derivable from the biomass itself (e.g., alcohol, ketone) or to water [12,13]. Karagoz et al. carried out low temperature (<553 K) liquefaction in water and investigated the effects of treatment conditions including catalyst, temperature and reaction time [14–16]. The thermal liquefaction of white birch wood and filter pulp was studied in water and methanol vapor at 2 MPa pressure in a flow-through reactor [17]. Demirbas reported wood and agricultural materials were delignified in either glycerol or alkaline glycerol in aqueous or non-aqueous media for the production of pulps [18]. Cemek et al. investigated the verbascum stalk liquefaction by supercritical fluid extraction and the resulting liquid product was divided into benzene and ethyl ether soluble fraction [19]. High conversions were realized on depolymerization of Kraft- and organosolv-derived lignin by KOH in supercritical methanol or ethanol was studied in rapidly heated batch microreactor and model compound studies confirmed that the dominant depolymerization route is the solvolysis of ether linkages [20]. Biomass liquefaction

* Corresponding author. Tel./fax: +86 10 62849515.

E-mail address: fszhang@rcees.ac.cn (F.-S. Zhang).

product is determined by various factors, including substrate type, heating conditions, solvent type, reactor configuration and catalyst.

To the best of our knowledge, solvolysis liquefaction of biomass has been carried out with some solvents, but the investigations cannot be compared due to the difference in the separation of products and definition of the liquid product and there is no studies carried out at identical conditions to understand the effect of solvent on the conversion rate, oil yield and product distribution. In the present paper we reported systematically the determination of solvent (water, ethanol and acetone) effect on the biomass liquefaction process. Especially for ethanol, biomass-to-ethanol fermentation produces a large quantity of lignin by-product, thus investigation of the ethanol on the biomass conversion (except fermentable fraction) is practicable to enhance the economic competitiveness of biomass-to-ethanol conversion. This work is part of our ongoing attempt to make a process to generate desired product more selective and controllable in the biomass liquefaction process.

2. Experimental

2.1. Materials

Biomass (pinewood) was obtained from a wood processing factory in Beijing suburb. The samples were firstly dried at 378 K for 24 h and then ground to less than 80 meshes. The chemical and elemental analysis of the pinewood sample was shown in Table 1. Ethanol, acetone and sodium sulfate were purchased from Beijing Chemicals Company (analytical grade) and used as received. The impurities in ethanol and acetone were identified through blank tests before experiments.

2.2. Solvolysis liquefaction process

The experiments were conducted in a 200 ml cylindrical autoclave made of 316 stainless steel and the autoclave can be operated at a maximum temperature of 873 K and maximum pressure of 65 MPa. In each test, the reactor was charged with 10 g pinewood and 60 g solvent and sealed. The air inside the autoclave was purged by argon gas for three times, then pressure in the autoclave was raised to 1 MPa with argon gas to avoid solvent vaporization. The reactor was heated to required temperature at 10–13 K/min where it was maintained for 20 min with less than ± 5 K variation. After the treatment, an electric fan was used to quickly cool the reactor to room temperature.

The procedure for separation and extraction of reaction product was given in Fig. 1. Briefly, the gas was removed from the autoclave after the reactor was cooled to room temperature and then the autoclave was opened. The solid and liquid mixture was removed from the autoclave and acidified by concentrated HCl to pH ~ 2 –3 (for ethanol and acetone liquefaction tests, the solvent was firstly removed from the solid and liquid mixture in rotary evaporator and then 50 ml de-ionized water was added to the mixture before acidification). The solid and liquid in the mixture were separated by vacuum filtration. The liquid fraction was extracted with ethyl ether and the solid fraction was ultrasonically extracted with acetone. Ethyl ether and acetone extractants were removed in a rotary

Fig. 1. A brief scheme of the product separation and analysis approach.

evaporator and the corresponding fraction was weighted and designated as oil A and oil B, respectively. Solid residue was defined as acetone insoluble fraction. Water in the oil was removed by anhydrous sodium sulfate. The conversion rate and oil yield were calculated by the following two formulas:

$$\text{Conversion rate} = [1 - (\text{weight of solid residue})] / (\text{weight of the feedstock})$$

$$\text{Oil yield} = (\text{oil A} + \text{oil B}) / (\text{weight of the feedstock})$$

2.3. Analysis methods

Biomass derived oil (oil A and oil B) was analyzed by a gas chromatograph equipped with mass selective detector (GC–MS, Agilent 7890A/5975C, USA). Both injector and detector were kept at 553 K and the carrier gas He velocity was 1 ml/min. HP-5 column (5% phenyl methyl siloxane, 30 m $\times$ 250 μm $\times$ 0.25 μm) was used. In order to give good product separation, the oven program was 1 min isothermal at 313 K, followed by a heating rate of 6 K/min to final 553 K and hold 5 min at the final temperature. The injected volume was 1 μl with split ratio of 30/1. The elemental analysis was carried out using a flash EA1112 Elemental Analyzer. The solid residue was dried at 378 K for 24 h and analyzed using KBr pelletization method on a Nicolet Nexus 670 (USA).

3. Results and discussion

3.1. Effect of solvent type on conversion rate

Liquefaction of pinewood with three different solvents (water, acetone and ethanol) was studied under identical experiment conditions. Average conversion rates from three replicate tests were shown in Fig. 2. Among the three tested solvents, acetone had the best effect on the conversion in all the tested temperatures and the highest conversion rates were 74.2%, 69.4% and 75.9% with

Table 1
Elemental and chemical composition of the pinewood

Elemental analysis (wt.%)					Chemical composition (wt.%)				LHV
C	H	O	N	S	Cellulose	Hemicellulose	Lignin	Ash	(MJ/kg)
49.25	6.18	44.17 ^a	0.30	0.10	37	38	22	0.30	16.32

^a By difference.

Fig. 2. Effect of solvent type on pinewood conversion rate as a function of temperatures. Other conditions: reaction time 20 min, starting pressure 1 MPa.

ethanol, water and acetone as solvent, respectively. On the other hand, it was noted when the temperature was relative low (<623 K), water had the highest conversion rate. In a study on the cellulose liquefaction Jakab et al. reported that the temperature range of cellulose decomposition became wider and shifted to lower temperature with increasing water content of the solvent vapor [17]. Accordingly, the trend stemmed from quick decomposition of the cellulose and this explanation was confirmed by the FTIR analysis of the solid residue below (Fig. 4). The different conversion rate in liquefaction process may due to the polarity constant values of the solvent [21]. In biomass liquefaction process, ionic reactions as well as free radical reactions took place in the closed system including nucleophilic, electrophilic, elimination reaction [22,23]. It was known that most of these reactions are related to the polarity of the reaction system. Higher conversion rate was obtained in solvent with higher polarity. The dipole moment of water, ethanol and acetone at their critical point are about 1.8, 1.7 and 2.9 D, respectively. In addition, acetone can also act as a reaction substrate reacting with pinewood decomposition intermediates and the reactions of solid residue formation from decomposition intermediates were prevented resulting in high conversion rate.

3.2. Effect of solvent type on oil yield

Table 2 summarized the results of oil yield with water, ethanol and acetone as liquefaction solvents at various temperatures. The highest yields reached 18.6%, 26.5% and 20.0% at 573 K, 673 K and 673 K for the three tested solvents, respectively. It was observed that oil yield increased with increasing temperature up to a certain value (573 K for water and 673 K for ethanol and acetone) and decreased thereafter for all the tested solvents. This could be attributed to the result of the following competitive reactions: (1) formation of solid by cyclization, condensation and re-polymerization of the liquid products and formation of gases from degradation of the liquid products and (2) formation of liquid products by decomposition of the solid and aggregation of the gases. It could be concluded that the effect of enhanced temperature on the reaction (2) outweighed reaction (1) from the observation. In the present study, ethanol had the highest oil yield and the highest yield was

11.4% and 18.2% for oil A and oil B obtained at 673 K and 623 K, respectively. Consequently, considering the oil yield, the solvent efficiency in the biomass liquefaction can be sequenced as follows: ethanol > acetone > water.

3.3. Effect of solvent type on product distribution

Table 3 (oil A) and Table 4 (oil B) presented the identified compounds in the oils obtained from biomass liquefaction in the three solvents under a starting pressure of 1 MPa and at 623 K for 20 min (only compounds with more than 1% of total area were shown). The area% for each compound identified (defined by the percentage of the compound's chromatographic area out of the total area) and the total area% for all the listed compounds were also shown in the Tables. It can be seen that the product categories and abundance were greatly affected by the solvent type.

According to GC–MS analysis results, the main difference between oil A and oil B was boiling points of the constituted compounds. The compounds in oil A have lower boiling points with retention time less than 25 min. In oil A of the three tested solvents liquefaction, 2-methoxy-phenol, 2-methoxy-4-methyl-phenol, 1,2-benzenediol and 1-(4-hydroxy-4-methoxyphenyl)-ethanone could all be detected, while they had significantly different relative abundance (e.g., 1,2-benzenediol, 10.00%, 3.57% and 4.05% of total area for water, ethanol and acetone, respectively). The major compound was 2-methoxy-phenol (17.20%) for water liquefaction, while 2-methoxy-4-methyl-phenol (8.23%) for ethanol liquefaction and 4-methyl-1,2-benzenediol (9.49%) for acetone liquefaction. It can be seen that water liquefaction process favored the production of 2-methoxy-phenol and 1,2-benzenediol (17.20% and 10.00% respectively) while more substituted phenol and 1,2-benzenediol compounds were produced in acetone and ethanol solvent liquefaction. These results were in good agreement with our previous suggestion that acetone and ethanol could act as substrates which further reacted with pinewood decomposition fragment and as a consequence more substituted compounds formed.

As for oil B, it was viscous dark liquid at room temperature. Fig. 3 showed that, there was notable difference in term of peaks intension and major peaks between the spectra of acetone extracts from the three solvents. The ethanol liquefaction product showed more major peaks than water and acetone, that is, comparatively wider product distribution. For water liquefaction products, three major peaks appeared at about 11.44, 34.67 and 36.35 min identified as 2-methoxy-phenol, benzene-acetic acid, 4-hydroxy-3-methoxy-methyl ester and 1-PA acid [1-phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methyl)-methyl ester, (1R,4aS, 10aR)-] respectively and these three compounds accounted for about 34.41% of total peak area. The major compound for ethanol liquefaction was (*E*)-2-methoxy-4-(1-propenyl)-phenol (11.85%) with retention time 19.80 min. Acetone liquefaction products had medium peaks. The compound 3-methylene-2-pentanone was detected at 4.48 min (5.48%) and was not found at ethanol and water liquefaction process. Only five compounds with more than 1% area, namely 4-hydroxy-4-methyl-2-pentanone, 2-methoxy-phenol, 2-methoxy-4-methyl-phenol, 4-ethyl-2-methoxy-phenol and 1-PA acid were all present in the three tested solvents liquefaction process.

Table 2
Oil yields from pinewood liquefaction in the tested solvents at different temperatures

Solvent	523 K		573 K		623 K		673 K		723 K		The highest yield (oil A + oil B)
	A	B	A	B	A	B	A	B	A	B	
Oil (wt.%)											
Acetone	2.1	5.5	2.2	8.1	4.1	11.9	5.6	14.4	8.1	11.2	20.0
Water	3.0	7.3	4.0	14.6	4.2	13.2	3.8	12.4	2.2	4.9	18.6
Ethanol	1.9	4.4	2.9	10.8	3.3	18.2	11.4	15.1	4.2	15.3	26.5

Table 3

Major compounds in ethyl ether extractant analyzed by GC–MS

No.	RT (min)	Solvent (area%)			Compound name
		Water	Ethanol	Acetone	
1	4.16	–	4.13	–	Acetic acid, hydroxy-, ethyl ester
2	4.79	–	4.54	–	Propanoic acid, 2-hydroxy-ethyl ester
3	5.16	–	–	7.94	2-Methoxy-furan
4	5.16	1.44	–	–	2-Cyclopenten-1-one,
5	5.67	–	–	3.14	(+)-4-Amino-4,5-dihydro-2(3H)-furanone
6	6.82	1.76	–	–	2-Cyclopenten-1-one,2-methy-
7	6.83	–	3.12	–	Butanoic acid, 2-hydroxy-, ethyl ester
8	5.95	–	3.20	2.71	3-Furanmethanol
9	7.82	1.96	–	3.54	2,5-Hexanedione
10	8.27	1.26	–	–	2-Cyclopenten-1-one, 3-methy-
11	8.71	1.99	1.37	–	Phenol
12	9.14	–	1.11	–	Pentanoic acid, 2-hydroxy-ethyl ester
13	9.82	1.09	–	–	2(3H)-Furanone, 5-ethylidihydro-3-methyl
14	9.88	–	–	2.78	3-Methyl-2,4-hexanedione
15	10.08	–	2.52	1.06	1,2-Cyclopentanedione, 3-methyl-
16	10.39	–	–	1.27	3(2H)-Furanone, 2-hexyl-5-methyl-
17	10.56	–	1.14	–	1,3-Dioxolane, 2-methyl-2-propyl-
18	10.74	–	1.70	–	Pentanoic acid, 4-oxo-, ethyl ether
19	11.12	2.48	–	–	Phenol, 4-methyl-
20	11.17	–	–	2.92	Thiazole, 5-methyl-
21	11.18	–	3.80	–	Butanoic acid, (tetrahydro-2-furanyl) methyl ester
22	11.52	17.20	4.39	2.70	Phenol, 2-methoxy-
23	12.19	–	–	1.73	Hexanethioic acid, S-propyl ester
24	12.61	–	2.80	–	1,4-Benzenediol, 2-methoxy-
25	13.62	–	–	1.50	1,2-Benzenediol, 3-methoxy-
26	13.69	–	2.20	–	Butanedioic acid, diethyl ester
27	14.01	–	–	2.68	Trans-furfurylideneacetone
28	14.13	7.69	8.23	2.98	Phenol, 2-methoxy-4-methyl-
29	14.16	10.00	3.57	4.05	1,2-Benzenediol
30	15.07	–	1.93	–	1,3-Dioxepane, 5-methyl-2-pentadecyl
31	15.11	–	–	2.83	Sulfurous acid, butyl-cyclohexyl-methyl ester
32	15.33	–	–	1.16	Ethanone, 1-(2,5-dihydroxyphenyl)-
33	15.37	–	3.16	–	1,3-Dioxepane, 5-methyl-2-pentadecyl-
34	15.73	–	2.75	–	2-Furanmethanol, tetrahydro
35	15.85	1.72	1.65	–	1,2-Benzenediol, 3-methyl-
36	15.95	3.94	–	–	Hydroquinone
37	16.15	–	1.23	–	3-Buten-2-ol, 2-methyl-
38	16.35	3.07	–	9.49	1,2-Benzenediol, 4-methyl-
39	16.74	–	1.27	–	Butanoic acid, 3,3-dimethyl-2-(1-methylethyl)-, methyl ester
40	17.54	–	–	1.62	4-Hydroxy-3-methylacetophenone
41	17.68	4.25	–	–	1,4-Benzenediol, 2-methyl-
42	18.00	–	1.94	–	Phenol,2-methoxy-4-propyl-
43	18.01	–	1.12	–	Eugenol
44	18.23	2.02	–	–	1,2,3-Benztriol
45	18.25	–	2.98	–	4-Methoxycarbonyl-4-butanolide
46	18.71	–	–	1.59	1,4'-Bipiperidine
47	18.75	1.70	1.44	–	Vanillin
48	18.89	1.00	–	3.43	Ethanone, 1-(3-hydroxyphenyl)-
50	20.36	–	3.70	1.70	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-
49	20.43	–	3.48	–	2-Furancarboxylic acid, tetrahydro-3-methyl-5-oxo-
51	20.59	1.64	1.19	8.00	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-
52	20.65	–	–	1.09	Ethanone, 1-(3-hydroxy-4-methoxyphenyl)-
53	21.52	3.80	2.72	–	Homovanillyl alcohol
54	21.82	–	–	2.26	Benzoic acid, 2,3-dihydroxy-
55	22.152	–	–	1.02	Pyrrolidine, 1-(1-cyclopenten-1-yl)-
56	24.35	3.60	–	–	4-Amino-2-hydroxytoluene
57	24.72	5.80	4.77	2.75	Benzenecetic acid, 4-hydroxy- 3- methoxy-
Total area		79.43	83.18	77.92	

– Not detected or peak area less than 1% of total area.

The pinewood liquefaction oil was a quite complex mixture. It can be seen from Table 3 and Table 4 that: (1) the most constituted compounds were phenol derivatives hydrocarbon and (2) solvent type markedly affected the product distribution. In contrast to acetone and ethanol, solvent water liquefaction products had the shortest product distribution range with only 44 compounds (area >1%) identified in the oil product. When ethanol was employed as solvent, many products fall on the methyl- or ethyl-ester compounds. Some ester compounds' formation could be suggested according to the previous reports [17,18,20,24,25]. For instance, butanoic acid, (tetrahydro-2-furanyl)-methyl ester possibly pro-

duced via esterification reaction between solvent ethanol derived butanoic acid and tetrahydro-2-furanmethanol. And some compounds, e.g., *trans*-furfurylidene acetone generated in the solvent acetone liquefaction process were through aldol condensation reaction between solvent acetone and biomass-derived 3-furanmethanol.

It was worthily noted that less compounds with nitrogen and sulfur atom were detected in the oils obtained in the present study compared with previous reports [14–16]. The lower heteroatom content may relate to the higher temperature (623 K). The higher temperature gave rise to thorough decomposition of heteroatom-

Table 4

Major compounds in acetone extractant analyzed by GC-MS

No.	RT (min)	Solvent (area%)			Compound name
		Acetone	Water	Ethanol	
1	4.48	5.48	–	–	2-Pentanone, 3-methylene
2	5.35	1.50	1.49	1.75	2-Pentanone, 4-hydroxy-4-methyl-
3	7.35	1.01	–	–	2,5-Hexanedione
4	8.24	–	1.01	–	2-Cyclopenten-1-one, 2-methyl-
5	11.02	1.27	1.18	–	Phenol, 3-methyl-
6	11.17	–	–	1.32	Butanoic acid, (tetrahydro-2-furanyl)methyl ester
7	11.44	1.57	9.83	2.14	Phenol, 2-methoxy-
8	13.40	1.20	–	–	2-Butanone, 4-(5-methyl-2-furanyl)
9	23.67	–	–	1.41	Butanedioic acid, diethyl ester
10	13.84	1.93	–	–	<i>Trans</i> , furfurylidene acetone
11	14.00	2.15	5.30	3.06	Phenol, 2-methoxy-4-methyl-
12	14.11	1.42	–	–	<i>Trans</i> -2-(1-hydroxycyclohexyl)-furan
13	15.36	–	–	1.22	4-Methylurazole
14	15.98	3.79	4.27	5.78	Phenol, 4-ethyl-2-methoxy-
15	16.04	2.84	–	–	Benzene, 1,4-dimethoxy-2-methyl-
16	16.64	2.03	–	–	Ethanone, 1-(2-hydroxy-5-methylphenyl)-
17	17.79	1.04	–	2.31	Eugenol
18	18.01	2.48	–	5.37	Phenol, 2-methoxy-4-propyl-
19	18.65	1.00	1.06	–	Ethanone, 1-(3-hydroxyphenyl)-
20	18.69	–	1.38	–	Vanillin
21	18.89	1.32	–	–	1,4-Benzenediol, 2,6-dimethyl-
22	19.80	4.54	–	11.85	Phenol, 2-methoxy-4-(1-propenyl)-(E)
23	20.53	1.25	–	–	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-
24	21.43	–	1.06	1.06	6-Amino-2,4-dimethylphenol
25	21.45	–	4.11	1.59	Benzene acid, 4-hydroxy-3-methoxy-
26	22.53	–	–	1.21	Benzoic acid, 4-hydroxy-3-methoxy-ethyl ester
27	23.77	–	1.32	4.15	Benzene,1,1'-(1,3-propanediyl)bis-
28	23.78	1.12	–	–	Homovanillyl alcohol
29	24.35	–	–	1.78	Benzene, 1,1'-(1-methyl-1,3-propanediyl)bis-
30	28.77	–	1.36	–	2,4-Dihydroxyphenyl-2-phenyl ethyl ester
31	30.74	–	–	1.52	2,3-Dimethyl-1,4,4a,9a-tetrahydroanthracene-9,10-dione
32	31.79	–	1.34	–	2-(1-Hydroxyisoamyl)-1-methoxy benzene
33	31.85	1.28	–	–	10,18-Bisnorabieta-5,7,9(10),11,13-pentaene
34	31.86	–	–	2.12	3',4'-Diisopropylbiphenyl
35	31.89	–	1.66	–	9-Octadecenoic acid, (E)-
36	32.16	–	–	1.84	Linoleic acid ethyl ester
37	32.25	–	–	3.24	Ethyl oleate
38	32.61	–	–	1.36	1-[4-(2- <i>p</i> -Tolyvinyl)phenyl] ethanone
39	33.08	–	1.81	1.26	Phenanthrene,1-methyl-7-(1-methylethyl)-
40	33.29	–	1.16	–	4,4'-Thiobis(2-methylethyl)-
41	34.24	–	–	5.61	4-Methoxy-2-hydroxy stibene
42	34.30	4.29	–	–	9 <i>H</i> -xanthen-9-one,2-methoxy-
43	34.50	–	1.51	–	Butanoic acid,4-[1-(oxobutyl)amino]phenyl ester
44	34.51	1.08	–	1.49	Phenol, 3-amino
45	34.67	–	7.95	2.39	Benzenacetic acid, 4-hydroxy-3-methoxy-, methyl ester
46	34.68	2.16	–	–	Propan-2-one, 1-(4-isopropoxy-3-methoxyphenyl)-
47	34.79	1.43	–	–	4,4'-Diacetyldiphenylmethane
48	34.86	–	1.42	–	Benzaldehyde acid, 3-[4(1,1-dimethylethyl)phenoxy]-
49	34.88	1.88	–	6.63	Phthalic acid, di(3-methylphenyl)ester
50	35.35	–	–	2.26	Methanone, (3,4-dimethylphenyl)(2,4,6-trimethylphenyl)-
51	36.06	–	–	1.64	Phenol, 4,4'-methylenebis[2,6-dimethyl]-
52	36.35	9.25	16.63	9.38	1-Phenanthrenecarboxylic acid, 1,2,3, 4,4a,9,10,10a-octahydro-1,4a-Dimethyl-7-(1-methyl)-, methyl ester,(1 <i>R</i> ,4 <i>aS</i> ,10 <i>aR</i>)-
53	37.98	–	–	1.44	4,4'-Dimethoxy-biphenyl-2-carboxylic acid,methyl ester
54	38.81	–	1.18	2.70	10,11-Dihydro-10-hydroxy-2,3-dimethoxydibenz(b,f)oxepin
55	38.84	2.53	–	–	6 <i>H</i> -Dibenzo[b,d]pyran-6-one,3,7dihydro-9-methoxy-1-methyl-
56	42.10	–	–	2.61	4-Methoxy-benzenmethanol
57	42.16	2.37	–	–	Benzeneacetic acid, 4-hydroxy-3- methoxy-,methyl ester
58	42.17	–	5.92	–	Benzeneethanamine, 3-hydroxy-4-methoxy-
59	44.38	–	2.01	–	2 <i>H</i> -1-benzopyran-2-one,4,5,7-trimethoxy-3-(4-methoxyphenyl)-
Total area		65.21	75.96	93.48	

– Not detected or peak area less than 1% of total area.

containing polymer (e.g., protein) and the elimination of heteroatoms like nitrogen, sulfur and so on.

3.4. FTIR analysis of the solid residue

The FTIR spectra of the raw pinewood and the solid residues after liquefaction with three tested solvents were shown in Fig. 4. According to the literature [26], the bands in the spectra of raw pinewood were assigned as follows. The bands at 3390 cm^{−1}

was caused by -OH in pinewood and water. Absorption at 2920 cm^{−1} was attributed to the symmetric CH₃-vibration of methoxy group and the band at 1060 cm^{−1} represented the C–O stretch vibration for the O–CH₂. The band at 1600 cm^{−1} and bands from 1400 cm^{−1} to 1640 cm^{−1} belonged to the aryl group (1600 cm^{−1} for the benzene backbone vibration). The presence of the C=O was suggested by the absorption at 1640 cm^{−1}. The reason for the broad band at 3390 cm^{−1} was contributed to the combination and overlap of absorption of aliphatic and aromatic O–H,

Fig. 3. GC-MS spectra of oil B from the tested solvents. Conditions: temperature 623 K, reaction time 20 min, starting pressure 1 MPa.

Fig. 4. FTIR spectra of the feedstock and residues liquefied by (a) water, (b) acetone and (c) ethanol. Conditions: reaction time 20 min, starting pressure 1 MPa, temperatures 1 – feedstock, 2 – 523 K, 3 – 573 K, 4 – 623 K, 5 – 673 K and 6 – 723 K.

Ar–H, =C–H and N–H stretching. The peaks between 1000 cm^{-1} and 600 cm^{-1} were from the out-of-plane vibrations of methyl or other alkyl constituents on the aromatic group. The pinewood is mainly constituted of cellulose, hemicellulose and lignin. From the analysis of the band above, it can be concluded that the band at 1640 cm^{-1} (C=O) represents the hemicellulose. The absorption at 1060 cm^{-1} represents the cellulose (β glycosidic bond) and absorption at 1400 cm^{-1} and 1600 cm^{-1} (benzene ring) represents the lignin.

The band at 1640 cm^{-1} almost disappeared after 523 K liquefaction showing that hemicellulose's decomposition preceded lignin and cellulose in all tested solvents. Solvent's effect on pinewood liquefaction can be clearly seen from the cellulose decomposition. As seen from Fig. 4, water compared with acetone and ethanol gave priority to cellulose decomposition at lower temperature (about 573 K) and this can be confirmed by the substantial decrease of absorption intensities of cellulose. Relative higher content of cellulose can be confirmed by high intensity of band at 1060 cm^{-1} when ethanol and acetone as solvent after 623 K liquefaction. The disappearance of bands at 1640 cm^{-1} and 1060 cm^{-1} showed the cellu-

lose and hemicellulose was almost totally transformed after 673 K liquefaction except in ethanol solvent. The only weak absorption at 1400 cm^{-1} and 1600 cm^{-1} bands implied the existence of lignin fragments in the solid residue besides solid carbon. It can be seen that the decomposition velocity of cellulose, hemicellulose and lignin was different in tested solvents resulting in different product category and relative abundance.

4. Conclusions

Liquefaction of biomass with proper solvents is a process that can promisefully be integrated with optimized conditions to simultaneously produce fuel additives and valuable chemicals. In the present study, the highest conversion rate was obtained when acetone was employed as liquefaction solvent and the maximum oil yield was found to be 26.5% in ethanol liquefaction process. The product distribution was also strongly affected by the solvent type. The major hydrocarbons were 2-methoxy-phenol, 1-PA acid and 4-hydroxy-3-methoxy-benzeneacetic acid in the case of water liquefaction process. The composition of oil from acetone

liquefaction process consisted mainly of 1-PA acid, 2-methoxy-furan, 4-methyl-1,2-benzenediol-1-(4-hydroxy-3-methoxy-phenyl)-ethanone. While solvent ethanol was favorable for the formation of (*E*)-2-methoxy-4-(1-propenyl)-phenol and 2-methoxy-4-methyl-phenol. The solid residue mainly consisted of solid carbon with little amount of lignin fragments at 723 K. The study has shown that employing different solvents could change the distribution and relative abundance of produced compounds. Further research is needed to select effective solvent with proper catalyst to narrow the product distribution and produce desired compounds to make the process more industrial.

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