Influence of methanol additive on bio-oil stability

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Abstract: Methanol at different mass concentrations (1, 6, 11, 16, 21 wt %) was added into crude bio-oil to upgrade oil properties. Indexes including pH value, water content and viscosity were measured regularly during a storage period of 91 days. GC-MS analysis was conducted before and after storage. An addition of 21 wt % methanol was found to improve the pH value from 2.97 to 3.88, and decrease the water content and viscosity after storage by 35.02% and 81.35%, respectively. The GC-MS analysis result convincingly showed that methanol could inhibit aging reactions such as polymerization and esterification which created new compounds in the oil. The FTIR and NMR analysis showed that methanol caused some structural changes in bio-oil.

Keywords: bio-oil, pyrolysis, stability, methanol

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1 Introduction

In contrast to fossil fuels, the biomass pyrolysis liquid product, bio-oil, which contains a low quantity of sulphur, nitrogen and ash, is considered as a clean energy source[1]. The biomass resource is abundantly available. The increase in atmospheric carbon dioxide which results from bio-oil combustion can be offset by photosynthesis[2]. For these reasons, using bio-oil can not only help solve the energy crisis, but also contribute to the alleviation of the greenhouse effect by reducing CO_2 emissions. However, the fuel quality of bio-oil is inferior to that of petroleum-based fuels and it is unsteady during storage[3]. Indexes such as density, water content and kinematic viscosity of crude bio-oil usually do not meet the specifications of the American Society for Testing and Materials (ASTM)[4]. The quality of bio-oil is influenced by material types and productive technology, while its poor stability is caused by the reactions among components, such as polymerization, esterification, alcoholization and aldolization[5,6].

Several methods have been proposed to improve the stability of bio-oil, e.g. hot-vapor filtration, solvent addition, emulsions, catalytic hydrogenation, etc[7]. Solvent addition is a relatively easy and economic way to improve some undesired properties of bio-oils. Many achievements have been obtained by using solvent.

Diebold et al.[8] studied the development of additives (10 wt % ethyl acetate; 5 wt % methyl isobutyl ketone and 5 wt % methanol; 10 wt %ethanol; 5 wt % acetone and 5 wt % methanol; 10 wt % acetone; and 10 wt % methanol) to stabilize the viscosity of bio-crude. Methanol was found as the best additive. The modified bio-crude was still a single-phase liquid and still met the ASTM No. 4 diesel fuel specification for viscosity even after 96 h when exposed to 90℃ with 10 wt % methanol

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content.

Britta Scholze[9] diluted bio-oil with methanol and afterwards distilled the solution. Thus the light reactive components were removed together with methanol and reactions of methanol with aldehydes might take place leading to the formation of acetales. The treated bio-oil had high stability and no sludge was developed at the bottom even after storing at 50℃ for more than two years.

Wu et al.[10] added ethanol and methyl acrylate at different mass concentrations (4 wt %, 8 wt %, 12 wt %, 16 wt %, 20 wt %) into bio-oil during a storage period of 42 days at 25℃. It showed that both ethanol and methyl acrylate had significant effects on improving the physicochemical properties of bio-oil. It was also observed that the effect of ethanol was superior to that of methyl acrylate at the same mass concentration.

Adding solvent into bio-oil may reduce reaction rate, lower bio-oil viscosity and improve its stability, which is considered as an effective way to upgrade the bio-oil[7]. Based on previous studies, this study aimed to add methanol at different mass concentrations into bio-oil and investigate its effect on the bio-oil physicochemical properties with storage. Compositional changes of pyrolysis oils were investigated by gas chromatographic-mass spectrometric (GC-MS), Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR).

2 Methods

2.1 Bio-oil

The bio-oil used here was produced from the fast pyrolysis of rice straw at 600℃ in a fluidised-bed reactor. After production, the bio-oil was sealed in glass bottles and temporarily stored in a freezer at 4℃ before further use.

2.2 Experimental procedure

Density, higher heating value (HHV) and ash content of the crude bio-oil were tested at first. Bio-oils mixed with methanol (typically reagent-grade quality) at different mass concentrations (1, 6, 11, 16 and 21 wt %) were sealed into 50 mL glass vials at 25℃ for 91 days. Due to the fact that the reactions were intense at first and slowed down afterwards, changes to the bio-oil physicochemical properties (pH value, water content and kinematic viscosity) with storage were tested every 7 days during the first 35 days and every 14 days during the later 56 days. Each test of pH, water content, and viscosity was repeated three times and the average value was used. GC-MS, FTIR and NMR analyses were conducted pre and post storage.

2.3 Analytical methods

The density was measured by digital density meter (ASTM D4052-11) from Anton Paar Co., Ltd., type DMA 4100M. The HHV was analyzed according to bomb calorimeter method (ASTM D240-92) by using an oxygen bomb calorimeter from Shanghai Changji Gealogical Instrument Co., Ltd., type XRY-1B. The ash content was tested according to ASTM D482-2007 using the ash content apparatus from Shanghai Shenkai Petroleum Instrument Co., Ltd., type SYP1005-I. The pH value was determined according to the pH-potentiometer method using a pH meter from Shanghai Leici Instrument Plant, type PHS-3C, and the particular electrode was from the same plant, type 65-1C. The water content was analyzed according to Karl Fisher reagent-volumetric method (ASTM E203-08) using Karl-Fischer titration from Metrohm Instrument Co., Ltd., type KFT 870. The kinematic viscosity was tested according to capillary method through viscometer (ASTM D445) by a petroleum products kinematic viscosity tester from Shanghai Changji Gealogical Instrument Co., Ltd., type SYD-265H.

GC-MS analysis was carried out by GC-MS analyzer from Perkin Elmer Company, type AutoSystem XL GC/TurboMass MS using a quadruple detector and a DB-5MS capillary column (30 m×0.25 mm inner diameter ×0.25 μm thickness). The oven temperature is programmed from 333 (4 min) to 513 K at a heating rate of 4 K/min, then to 573 K held at a heating rate of 20 K/min, and hold at 573 K for 13 min.

FTIR analysis was carried out by Fourier infrared and Raman spectrometer EQUINOX 55 from Bruker Company in the transmission mode between 4 000 cm^{-1} and 400 cm^{-1}. Dried KBr was used to prepare pellets.

NMR analysis was carried out to determine the percentage of functional groups in bio-oil by nuclear magnetic resonance instrument from Bruker Company, type AvanceIII400. A total of 0.10 g of bio-oil was dissolved in 0.5 mL of $CDCl_3$ which contained 0.03% (v/v) tetramethylsilane (TMS) as an internal reference. The H spectra of bio-oil were acquired at 400 MHz, with a 90 pulse angle and a sweep width of 4 000 Hz.

3 Results and discussion

3.1 Bio-oil

The crude bio-oil is a single-phase sticky liquid with a dark brown appearance and a pungent smell. The density of the bio-oil was 1.16 g/mL. Its HHV was 16.31 MJ/kg which was about 40%-50% of conventional fuel oils. It is reported that there are some relationship between ash and the corrosivity of the bio-oil. The ash content has positive correlation with corrosivity[11]. According to the experiment, the ash content was 0.19 wt %, which was relatively low.

3.2 pH value

Bio-oils contain substantial amounts of organic acids, mainly acetic and formic acid, which result in a pH value between 2.0 and 3.0[12]. Figure 1 showed the pH value (25℃) of the bio-oil stored for 91 days. It showed that bio-oil had a pH value of 2.97-3.88.

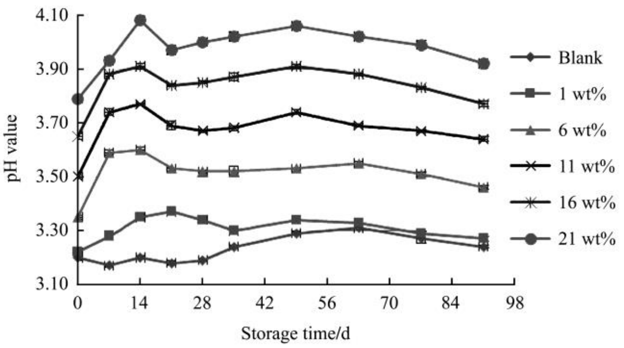

Figure 1 pH value (25℃) of the bio-oil stored for 91 days

The acid number is very high and it is even higher at high temperature. For this reason the oils are corrosive to common construction materials such as carbon steel, aluminum and nickel[13,14]. So it is very important to improve the pH value of the bio-oil.

Figure 1 shows that the pH value was improved with the addition of methanol. This was a prompt effect and could maintain to the end of storage. Compared to the blank, the pH value of the rest groups increased with methanol concentration by 0.67%, 5.00%, 10.00%, 15.00% and 19.67%, respectively before storage (day 0). After storage (day 91), the percentage~~s~~ increased to 0.99%, 7.24%, 13.16%, 17.43% and 22.37%, respectively.

According to the literature, the pH value of the bio-oil is stable in the early stages of storage[15]. It is also reported that there is a certain relationship between the pH value and the water content of bio-oil[16]. Figure 1 showed that the pH value of the blank did not change so much during the first 28 days from 3.00 to 2.99, from which the change in water content could be speculated.

As a neutral solvent, methanol was added into the bio-oil and the physical dilution changed the sour environment of bio-oil, so the pH value was increased immediately with methanol. Methanol can react with the organic acid components of the bio-oil, which resulted in an increase of the pH value during the prior 14 days. However, the acidification tendency was not changed with the consumption of the methanol. A. Oasmaa et al indicated that the chemical reactions that can occur between the bio-oil and methanol or ethanol are esterification and acetalization. Though thermodynamically non-favored, they can proceed to a significant extent if appropriate conditions are applied[3].

Tukey's multiple comparison method based on the DPS data processing software was used to analyze the effects of the methanol concentration and the storage time on the pH value. It showed that there were highly significant differences (all of the levels of significance mentioned are 1%) among the effects of different methanol concentrations, while differences between the storage time were significant. The decrease in efficiency in order was 21, 16, 11, 6, 1 wt % and the blank. Therefore, it could be inferred that the best concentration to improve the pH value was 21 wt %.

3.3 Water content

In their study on the stability of pyrolysis bio-oils, Czernik et al. reported that the water concentration in the bio-oil increased with storage time[17]. In this study, the water content measurements showed the same tendency with storage time. Figure 2 showed the water content of the bio-oil stored for 91 days.

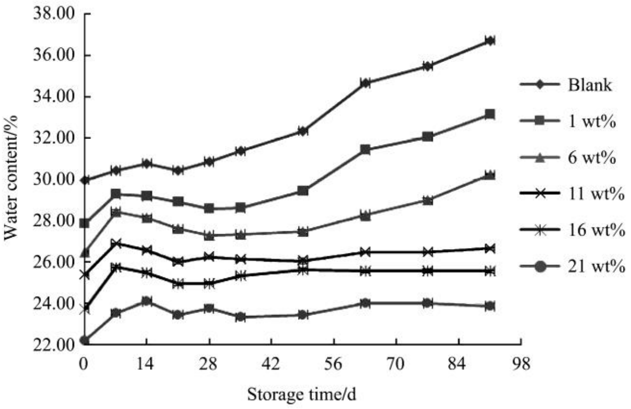

Figure 2 Water content of the bio-oil stored for 91 days /wt %

The result showed that the water content in crude bio-oil increased with time and was high. The presence of water contributes to the phase separation and greatly lowers its heating value[3,18]. So it is of great significance to lower the water content.

According to Figure 2, the water content was reduced with the addition of methanol. It was a prompt effect and was maintained to the end of storage. Compared to the blank, the water content of the methanol treated groups decreased by 6.98%, 11.67%, 15.32%, 20.78% and 25.87%, respectively before storage (day 0). After storage (day 91), the decreasing rate reached 9.83%, 17.73%, 27.45%, 30.42% and 35.02%, respectively.

Water content was steady for all groups within the early 28 days. Combined with the same variation of the pH value and the constantly increasing viscosity in Figure 3, it can be inferred that the reaction occurred during this time was mainly polymerization. Etherification, esterification and aldolization occurred between hydroxyl, carbonyl, and carboxyl group components, in which water was formed as a byproduct [17,19].

The variation of water content in each methanol treated group was not exactly the same. The chemical reactions between the solvent and the oil components occurred quickly for the prior 7 days, so the water content increased in each group. The water content of the 11, 16 and 21 wt % groups maintained a steady level because the alcohols can reduce the further reaction rate by changing the oil microstructure or by the formation of acetal[3,19]. As for the 1 and 6 wt % groups, the methanol was not enough to inhibit the aging reactions after 28 days. Anja Oasmaa et al. drew a similar conclusion in their study, reporting that with low (≤5 wt %) alcohol additions, the aging reactions were prevented for a few months, while with higher (≥10 wt %) alcohol additions, the aging reactions were delayed for almost 1 year[19].

Tukey’s multiple comparison method based on the DPS data processing software was used to analyze the influences of the methanol concentration and the storage time on the water content. Results showed that there were no significant differences between the 11 and 16 wt % groups and the rest were significantly different between one and another. The decrease in efficiency in order was 21, 16 (or 11), 6, 1 wt %, and the blank. Also, differences between the storage times were significant. Therefore, it was postulated that the best concentration of methanol to control the water content was 21 wt %.

3.4 Viscosity

The increase of bio-oil kinematic viscosity with time is an important indicator to measure the degree of aging[1]. Polymerization, esterication and etherication were among the reactions that could be responsible for the significant rise of the viscosity of the bio-oils during their storage[20]. Figure 3 showed the viscosity (40℃) of the bio-oils stored for 91 days.

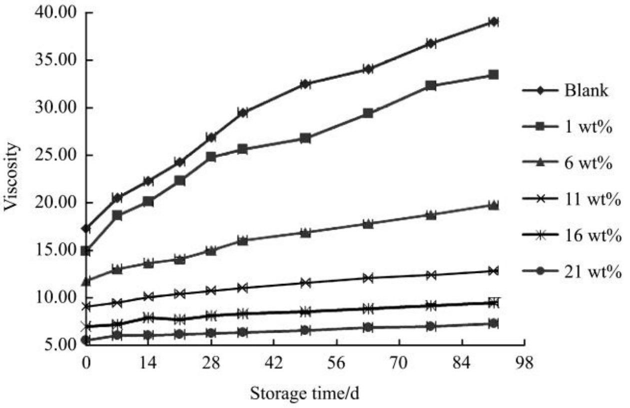

Figure 3 Viscosity (40℃) of the bio-oils stored for 91 days /mm^2/s

The increase of viscosity with time is not desired because this increases the difficulty and cost of atomization for combustion[8]. Figure 3 showed that the viscosity decreased with the addition of methanol. Compared to the blank, the viscosity of the treated groups decreased by 13.52%, 31.63%, 47.31%, 59.29% and 67.84%, respectively before storage (day 0). After storage (day 91), the decreasing percentages were 14.19%, 49.33%, 67.06%, 75.75% and 81.35% respectively.

Adding methanol can not only decrease the initial viscosity, but also decrease its increasing ratio. This is achieved through three main mechanisms: (1) physical dilution; (2) lowering the reaction rate or by changing the oil microstructure; and (3) reacting with the components to stop further chain growth[3,8]. In addition, due to acetal formation, aldehydes and ketones might be protected from further reactions[19].

Tukey's multiple comparison method was used to analyse the influences of the methanol concentration and the storage time on the viscosity. Results showed that there were no significant differences between the 11, 16 and 21 wt % groups and highly significant differences among the rest. The decrease in efficiency in order was 21 (16 or 11), 6, 1 wt %, and the blank. Again, differences between the storage times were significant. Obviously, the properties were improved with greater amounts of addition. However, with an auxiliary component, less addition with good efficiency was expected. As adding more methanol could not significantly reduce the viscosity, it was considered that the ideal concentration on viscosity was 11 wt %.

3.5 GC-MS analysis

GC-MS analysis was carried out to identify the changing compounds in the bio-oils. Compounds of 1, 6, 11, 16, 21 wt % methanol (day 0) groups were almost the same as that of the blank (day 0), which was omitted. There were 48, 65, 68, 69, 69, 67 and 63 compounds detected for the blanks (day 0 and day 91), 1, 6, 11, 16 and 21 wt % methanol (91th day) groups, respectively. Table 1 illustratee the compounds of the bio-oils by GC-MS in which the compounds were divided into five types (type A (No.1-7), B (No.8-16), C (No.17-48), D (No.49-71), E (No.72-84)) according to the different groups in which they were detected[21].

Table 1 Compounds of the bio-oils by GC-MS

No.	Compounds	Retention time/min	Relative mass content/%						
			Blank (day 0)	Blank (91th day)	Methanol mass concentration				
					1 wt % (91th day)	6 wt % (91th day)	11 wt % (91th day)	16 wt % (91th day)	21 wt % (91th day)
1	2-Furanmethanol	4.62	1.07						
2	2-Hexene, 3-methyl-, (Z)-	8.251	0.93						
3	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	17.694	1.69						
4	Phenol, 2-methoxy-4-propyl-	25.031	0.20						
5	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	25.965	0.46						
6	Benzofuran, 2,3-dihydro-	17.072	4.89			1.05	1.12	1.42	1.85
7	2-Methoxy-4-vinylphenol	20.36	2.04		0.57	0.62	0.64	0.79	1.01
8	4-Methoxy-4',5'-methylenedioxybiphenyl-2-carboxylic acid	51.541	0.33	0.21					
9	2,5-Hexanedione	6.747	2.94	0.24	0.23				
10	4(1H)-Pyrimidinone, 6-hydroxy-	9.604	0.38	0.28	0.26				
11	2-Furancarboxylic acid	11.753	0.28	0.23	0.21				
12	2-Pentanone, 3-methyl-	4.751	1.36	0.54	0.53	0.48			
13	2-Cyclopenten-1-one, 2,3-dimethyl-	9.084	0.87	0.57	0.45	0.43			
14	4-Methyl-5H-furan-2-one	10.731	1.70	1.22	1.21	1.19			
15	Phenol, 2,4-dimethyl-	14.539	1.28	1.04	1.00	0.97	0.94		
16	2-Cyclopenten-1-one, 3-methyl-	7.939	1.47	1.36	1.31	1.31	1.08	0.78	
17	Furfural	4.208	7.06	5.31	4.88	4.66	4.03	3.82	3.36
18	1,2-Ethanediol, diacetate	5.011	2.59	1.96	1.96	1.47	1.43	1.38	1.36
19	2(5H)-Furanone	6.327	2.31	3.80	3.77	3.16	2.98	2.83	2.74
20	1,2-Cyclopentanedione, 3-methyl-	10.176	5.49	5.22	4.71	4.48	3.81	3.41	3.38
21	p-Creso	11.894	1.69	2.86	2.71	2.47	2.41	2.18	2.13
22	Phenol, 2-methoxy-	12.408	6.81	8.09	7.60	7.21	6.02	5.81	5.63
23	Maltol	13.258	1.10	0.80	0.78	0.73	0.77	0.71	0.68
24	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	13.506	0.34	1.02	0.94	0.84	0.79	0.73	0.73
25	2,3-Dihydroxybenzaldehyde	15.094	0.16	0.67	0.66	0.63	0.46	0.36	0.32
26	Phenol, 4-ethyl-	15.23	2.05	4.26	3.85	3.60	3.52	3.12	3.03
27	Creosol	16.162	2.94	5.13	4.90	4.40	3.85	3.33	3.29
28	Phenol, 2,6-dimethoxy-	21.629	0.87	2.31	2.24	1.82	1.78	1.75	1.60

No.	Compounds	Retention time/min	Relative mass content/%						
			Blank (day 0)	Blank (91th day)	Methanol mass concentration				
					1 wt % (91th day)	6 wt % (91th day)	11 wt % (91th day)	16 wt % (91th day)	21 wt % (91th day)
29	Eugenol	21.824	0.86	1.75	1.71	1.55	1.48	1.40	1.32
30	Vanillin	23.181	2.03	3.07	2.77	2.67	2.36	2.45	2.11
31	Phenol, 2-methoxy-4-(1-propenyl)-	23.459	2.15	1.43	1.41	1.23	1.18	1.16	1.05
32	2(5H)-Furanone, 5-methyl-	7.083	0.69	0.51	0.51	0.56	0.58	0.60	0.63
33	2-Furancarboxaldehyde, 5-methyl-	7.88	1.48	0.78	0.81	1.00	1.10	1.16	1.64
34	4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	31.257	0.29	0.31	0.30	0.41	0.46	0.47	0.48
35	Phenol	8.476	2.71	3.49	2.87	3.23	2.45	2.20	2.72
36	Phenol, 4-ethyl-2-methoxy-	19.185	1.36	2.68	2.63	2.40	2.05	1.87	2.14
37	2-Cyclopenten-1-one, 2,3-dimethyl-	10.554	0.53	0.41	0.40	0.44	0.39	0.34	0.34
38	Phenol, 2-methyl-	11.133	1.21	1.72	1.89	2.08	1.91	1.68	1.27
39	Phenol, 2-ethyl-	14.185	0.41	0.32	0.35	0.37	0.30	0.27	0.26
40	Catechol	16.452	3.32	3.07	2.80	2.99	3.32	3.96	3.63
41	1,2-Benzenediol, 3-methoxy-	18.541	1.02	1.32	1.29	1.29	1.24	1.29	1.33
42	1,2-Benzenediol, 4-methyl-	19.592	0.99	0.95	0.97	0.46	0.91	0.93	0.88
43	Benzaldehyde, 4-hydroxy-	22.001	0.45	0.64	0.71	0.65	0.44	0.41	0.58
44	4-Ethylcatechol	22.691	0.53	0.58	0.51	0.32	0.53	0.59	0.43
45	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	30.968	0.20	0.41	0.46	0.49	0.32	0.33	0.35
46	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	32.09	0.56	0.57	0.71	0.74	0.70	0.79	0.70
47	2-Propenal, 3-(4-hydroxy-3-methoxyphenyl)-	32.957	1.21	2.14	2.66	2.76	1.92	1.95	1.79
48	2-Propenoic acid, 3-(4-hydroxyphenyl)-, methyl ester	33.3	0.25	0.20	0.26	0.27	0.13	0.25	0.12
49	n-Hexadecanoic acid	38.678		1.01	0.96	0.94	0.75	0.75	0.57
50	Oleic Acid	42.751		0.58	0.57	0.56	0.46	0.41	0.33
51	Benzoic acid, 4-hydroxy-3-methoxy-	24.693		0.97	0.70	0.63	0.55	0.26	
52	3,5-Dimethoxy-4-hydroxyphenylacetic acid	33.996		0.29	0.30	0.30	0.20	0.18	
53	12-Ethylsophoramine	51.535		0.61	0.78	0.75	0.56	0.48	
54	Phenol, 4,4'-methylenebis[2,6-dimethoxy-	52.102		0.47	0.44	0.40	0.31	0.24	
55	2,3-Dimethoxytoluene	17.815		0.29	0.28	0.26			
56	2-Furanone, 2,5-dihydro-3,5-dimethyl	12.095		0.41	0.42				
57	2-Cyclopenten-1-one, 2-methyl-	6.085		0.59	0.80	0.68	0.72	0.78	0.69
58	Benzaldehyde, 3-hydroxy-	20.177		0.37	0.45	0.43	0.49	0.44	0.45
59	1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	16.77		0.81	0.89	1.10	1.13	1.41	1.79
60	trans-Isoeugenol	24.764		1.71	2.25	2.41	2.46	2.68	2.74
61	Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	26.836		0.22	0.32	0.35	0.42	0.59	0.71
62	Phenol, 2-methoxy-3-methyl-	15.637		0.48	0.51	0.54	0.49	0.49	0.50
63	2-Methoxy-5-methylphenol	15.897		0.26	0.27	0.24	0.23	0.19	0.25
64	Benzene, 1-ethyl-4-methoxy-	17.762		0.36	0.35	0.34	0.32	0.28	0.31
65	Phenol, 4-propyl-	18.447		0.35	0.36	0.36	0.29	0.26	0.32
66	Ethanone, 1-(2,4-dihydroxyphenyl)-	19.031		0.36	0.34	0.35	0.25	0.23	0.32
67	Phenol, 2-methoxy-4-propyl-	22.137		0.61	0.64	0.54	0.54	0.62	0.47
68	Apocynin	25.903		1.06	1.02	0.97	1.23	1.41	1.16
69	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	29.368		0.33	0.32	0.31	0.24	0.25	0.22
70	Homovanillic acid	30.62		0.46	0.57	0.50	0.37	0.38	0.44
71	2-Propenoic acid, 3-(4-hydroxy-3-methoxyphenyl)-, methyl ester	35.661		0.21	0.19	0.22	0.14	0.15	0.16
72	Glycolaldehyde dimethyl acetal	3.488				1.33	1.85	3.91	4.77
73	Furan, tetrahydro-2,5-dimethoxy-	5.312				1.32	2.16	2.64	3.16
74	Phenol, 4-(2-propenyl)-	21.263				0.21	0.27	0.30	0.33
75	Hexadecanoic acid, methyl ester	37.828				0.28	0.28	0.32	0.42
76	1,2-Cyclopentanedione	6.57					0.28	0.28	0.32
77	2(5H)-Furanone, 3-methyl-	8.4					0.26	0.41	0.44
78	Acetophenone	11.528					0.32	0.31	0.32
79	9-Octadecenoic acid, methyl ester,	41.925					0.22	0.26	0.31
80	Benzene, 1,2,3-trimethoxy-5-methyl	27.125			0.26	0.24	0.22	0.21	0.24
81	5-Hydroxymethylfurfural	17.491			0.79	0.82	0.80	0.85	0.87
82	Stigmastan-3,5-diene	55.077			0.28	0.23	0.21	0.19	0.20
83	.gamma.-Sitosterol	57.586			0.38	0.33	0.35	0.34	0.37
84	5,9-Dodecadien-2-one, 6,10-dimethyl-, (E,E))-	4.71				0.47	0.48	0.48	0.46

Compounds in type A (No.1-7) were detected in blank (day 0) and part additive groups. They were the active reactants in aging reactions and would completely react during storage if the methanol was not added into bio-oil. Methanol with high concentration could inhibit some aging reactions (e.g. No.6-7). Compounds in type B (No.8-16) were detected in blank (day 0 and day 91) and most additive groups. Methanol could react with these compounds which can be completely consumed with the increased addition of methanol. Compounds in type C (No.17-48) were detected in all groups. Among them, for No.17-31, the content of compound was reduced compared to the blank (day 91). For No.32-34, the content of compound was increased compared to the blank (day 91). For No.35-48, the content of the compound had no obvious relationship with addition of methanol. Compounds in type D (No.49-71) were supposed to be the products of aging reactions. The presence of methanol had both negative (No.49-56) and positive (No.57-61) effects on the compounds. Content of compound No.62-71 had no relation with addition of methanol. Compounds in type E (No.72-84) were detected only in additive groups. They were speculated to be the products of reactions between the solvent and the oil components.

According to Table 1, lots of oxygenated compounds were detected, which was a direct cause of rather low heating value of pyrolysis bio-oil[22]. GC-MS analysis of both the blank and additive groups convinced that methanol could inhibit some aging reactions involved in the reactions bringing new compounds, resulting in a slightly increase of pH value, water content and viscosity when methanol was added compare with a fast increase of the blank with storage time.

3.6 FTIR analysis

Figure 4 illustrated the infrared spectroscopy result of pre and post storage of bio-oils. Before storage, only the blank was analyzed for the reason that methanol did not react with the bio-oil and there were no structural differences between the blank and the other groups. Table 2 indicated the infrared spectroscopy analysis result of bio-oils.

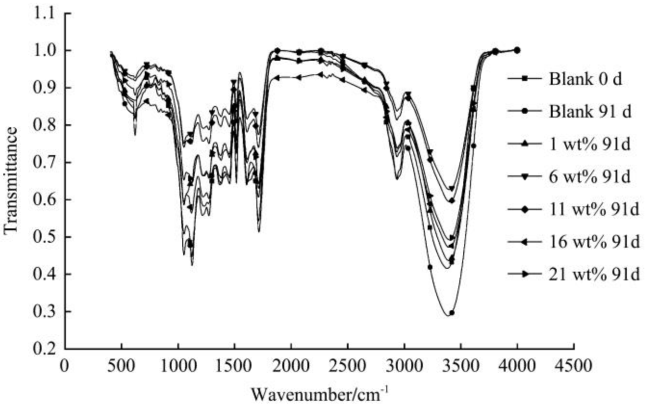

Figure 4 Infrared spectroscopy result of pre and post storage of bio-oils

Table 2 Infrared spectroscopy analysis result of bio-oils

Wavenumber/cm^{-1}							Functional groups	Compounds
Blank (0 d)	Blank (91 d)	1 wt% (91 d)	6 wt% (91 d)	11 wt% (91 d)	16 wt% (91 d)	21 wt% (91 d)		
3 377.95	3 386.38	3 392.76	3 398.59	3 399.42	3 396.00	3 396.58	O-H stretching vibration	alcohol, phenol
2 931.50	2 937.32	2 937.22	2 935.55	2 934.28	2 935.45	2 933.70	C-H stretching vibration	$-CH_3$
1 712.25	1 715.18	1 713.46	1 711.70	1 710.43	1 710.60	1 710.83	C=O stretching vibration	aliphatic ketone
1 606.43	1 613.70	1 610.67	1 609.93	1 609.29	1 609.16	1 608.67	C=O stretching vibration	carboxylic acid anionic
1 515.22	1 515.49	1 515.49	1 515.01	1 514.86	1 515.10	1 514.90	N-H flexural vibration	amino acid hydrochloride
1 455.90	—	—	1 454.08	1 454.85	1 454.24	1 454.71	C=C stretching vibration	aromatics
1 373.15	1 380.18	1 379.85	1 379.21	1 377.95	1 379.06	1 376.83	C-H flexural vibration	$-CH(CH_3)_2$
1 272.16	—	1 272.98	1 272.12	1 272.78	1 272.73	1 272.94	C-O stretching vibration	aromatic acid ester
1 215.31	1 230.78	—	—	—	—	—	C-O stretching vibration	phenol
1 120.37	1 123.02	—	—	—	1 118.09	1 118.32	C-O stretching vibration	saturation
1 052.47	1 051.23	1 051.70	1 051.65	1 051.60	1 051.94	1 051.69	C-O stretching vibration	ester of 1° alcohol
618.91	619.38	622.78	619.43	619.29	620.20	619.73	C-H flexural vibration	Alkyne

Each group had a strong absorption peak at 3 200-3 550 cm^{-1}, corresponding to O-H stretching vibration, indicating that there were large amounts of alcohols and phenols[23]. Absorption peaks at 2 872-2 962 cm^{-1} corresponded to C-H stretching vibration, suggesting the existence of $-CH_3$[24]. Absorption peaks at 1 705-

1 720 cm^{-1} were also very strong, corresponding to C=O stretching vibration, suggesting high content of aliphatic ketone[25]. Absorption peaks at 1 550-1 650 cm^{-1} corresponded to C=O stretching vibration, suggesting the existence of carboxylic acid anion[25]. Absorption peaks at 1 485-1 550 cm^{-1} corresponded to N-H flexural vibration, suggesting the existence of amino acid hydrochloride[25]. Absorption peaks at 1 400-1 500 cm^{-1} corresponded to C=C stretching vibration, suggesting the existence of aromatics[25]. Absorption peaks at 1 380-1 385 cm^{-1} corresponded to C-H flexural vibration, suggesting the existence of -$CH(CH_3)_2$[25]. Absorption peaks at 1 250-1 310 cm^{-1} corresponded to C-O stretching vibration, suggesting the existence of aromatic acid ester[25]. Absorption peaks at 1 180-1 260 cm^{-1} corresponded to C-O stretching vibration, suggesting the existence of phenol, which were only found in the blanks[25]. Absorption peaks at 1 031-1 064 cm^{-1} corresponded to C-O stretching vibration, suggesting the existence of ester of alcohol[25].

According to Figure 4, in O-H stretching vibration region which is located in 3 200-3 550 cm^{-1}, the peak of the blank on day 91 was much greater than that of the blank on day 0. This suggested that polymerization reaction of bio-oil occurred because there might exist intermolecular resonance hydrogen bonds during the storage[25]. The peak of O-H stretching vibration in blank (day 0) was higher than 1, 6, 11, 16 and 21 wt% methanol (day 91), which illustrates that adding methanol into bio-oil could inhibit the polymerization reaction. In aliphatic ketone region located in 1 705-1 720 cm^{-1}, absorption peaks of 1, 6, 11, 16 and 21 wt% methanol (day 91) are weaker than the blank (day 0) and the blank (day 91), which suggested that double bonds fraction was changed because of esterification and etherification reaction[24].

3.7 NMR analysis

Figure 5 illustrated the NMR spectroscopy results of pre and post storage of bio-oils. Comparing the NMR spectroscopy of pre and post storage of the blank, it can be observed that after storage, part peaks at 0.75-1.5 ppm disappeared corresponding to methyl and methylene functional groups linking to the far end of aromatic rings[26]. Peaks at 2.78 ppm appeared after storage corresponding to methyl and methylene functional groups linking to the near end of aromatic rings[27]. Peaks at 3.50 ppm disappeared corresponding to methylene linking to aromatic rings. Peaks at 4.50-4.88 ppm decreased corresponding to phenolic or olefin proton[28].

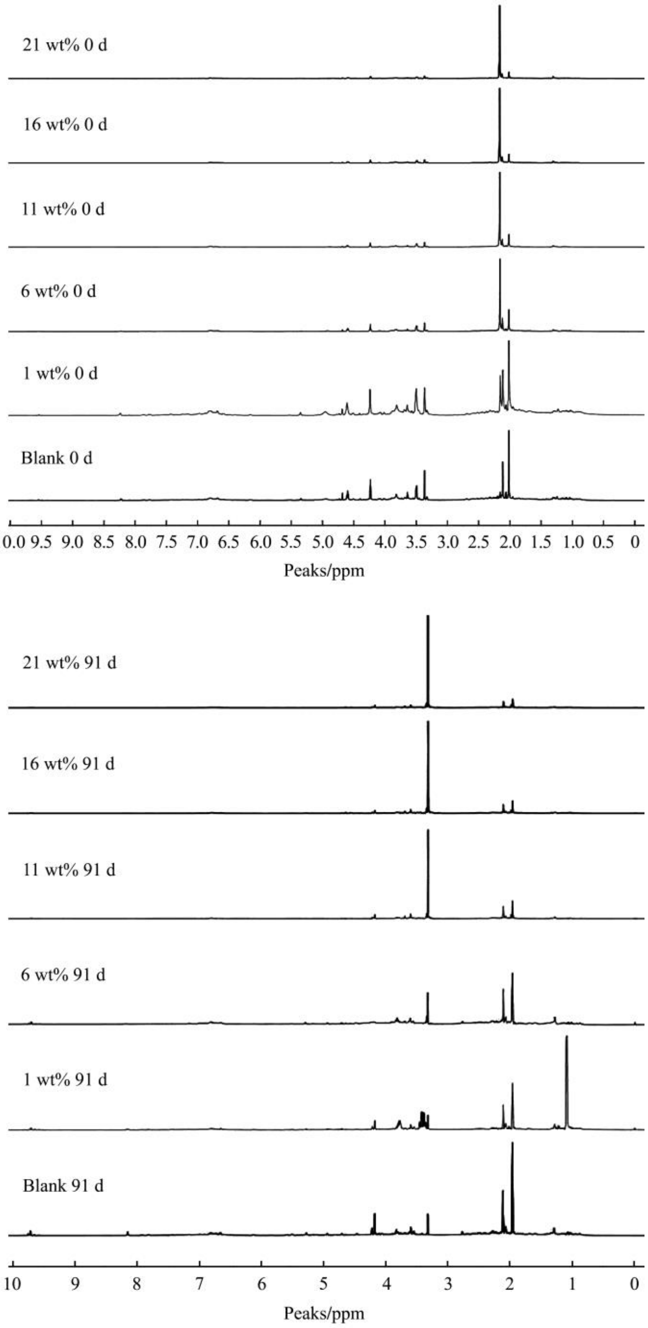

Figure 5 NMR spectroscopy result of pre and post storage of bio-oils

Comparing the NMR spectroscopy of pre and post storage of bio-oils with 1 wt% methanol, it could be seen that after storage peaks at 1.09 ppm appeared, indicating that adding methanol contributed to the forming of methyl at the far end of aromatic rings[26]. Peaks at

2.16-2.17 ppm, 3.30-4.30 ppm and 4.50-4.80 ppm were reduced, corresponding to methyl or methylene linking to aromatic rings, methylene connecting aromatic rings and phenol or furan, respectively[27].

Comparing the NMR spectroscopy of pre and post storage of bio-oils with 6 wt% methanol, it is shown that methyl was increased at 0.80-1.50 ppm. Methyl or methylene linking to the near end of aromatic rings at 1.80-2.50 ppm was decreased[27]. Methylene connecting aromatic rings at 3.30-4.50 was increased. Phenol or furan peaks at 4.50-4.80 ppm were reduced. The protons connecting aromatic rings of furan type at 6.50-7.50 were increased[28].

Comparing the NMR spectroscopy of pre and post storage of bio-oils with 11, 16 and 21 wt% methanol, it could be seen that in all the three groups, methyl or methylene linking to the near end of aromatic rings at 1.80-2.50 ppm decreased and methylene connecting aromatic rings at 3.30-4.50 increased after storage[26].

Comparing all the groups before storage, it could be seen that ethyl or methylene linking to the far end of aromatic rings at 2.02 ppm and linking to the near end of aromatic rings at 2.18 ppm increased with the concentration of methanol[26]. Methylene connecting aromatic rings at 3.30-4.50 decreased with the concentration of methanol[27].

Comparing all the groups after storage, it could be seen that ethyl or methylene linking to the aromatic rings at 1.96 and 2.11 ppm was decreased with the concentration of methanol[27]. Methylene connecting aromatic rings at 3.30 ppm increased with the concentration of methanol. Part peaks of the methylene connecting aromatic rings disappeared in the blank. Ethyl or methylene linking to the near end of aromatic rings at 1.80-2.50 ppm decreased with the concentration of methanol. Methylene connecting aromatic rings at 3.30-4.50 increased with the concentration of methanol.

According Figure 4 and Figure 5, the bio-oils underwent chemical and physical changes likely due to several reactions, including oxidation condensation and polymerization[29]. Oxidation condensation includes esterification and etherification. Polymerization can include reactions between species with double bonds[30]. The above reactions continue after bio-oil production because the reaction has not reached thermodynamic equilibrium after the rapid quenching of pyrolysis volatiles which is an important step for fast pyrolysis. The products continue to react during storage until stability is reached[6].

4 Conclusions

1) The pH value was improved, and the water content and viscosity were reduced with the addition of methanol which was a prompt effect and was maintained to the end of storage. The most efficient concentrations of methanol for pH value and water content were 21 wt%. The most ideal concentration for viscosity was 11 wt%.

2) GC-MS analysis of both the blank and additive groups convinced that methanol could inhibit some aging reactions involved in the reactions bringing new compounds. Lots of oxygenated compounds was detected, which was a direct cause of the rather low heating value of pyrolysis bio-oil

3) FTIR and NMR analysis of pre-storage and post-storage of bio-oils showed that the bio-oils underwent chemical and physical changes likely due to several reactions, including oxidation condensation and polymerization. The analysis illustrated that adding methanol could bring some structural changes in bio-oil.

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[References]

[1] Zhang Q, Chang J, Wang T J. Upgrading bio-oil over different solid catalysts. Energy and Fuels, 2006; 20: 2717－2720.

[2] Mohan D, Pittman C U, Jr H, Steele P. Pyrolysis of

wood/biomass for bio-oil: a critical review. Energy and Fuels, 2006; 20: 848－889.

[3] Oasmaa A, Czernik S. Fuel Oil Quality of biomass pyrolysis oils—state of the art for the end users. Energy and fuels, 1999; 13: 914－921.

[4] Bridgwater A V, Meier D, Radlein D. An overview of fast pyrolysis of biomass. Organic Geochemistry, 1999; 30: 1479－1493.

[5] Li W, Pan C Y, Zhang Q J, Liu Z, Peng J, Chen P, Lou H, Zheng X M. Upgrading of low-boiling fraction of bio-oil in supercritical methanol and reaction network. Bioresource Technology, 2011; 102: 4884－4889.

[6] Diebold J P. A Review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils, Colorado. 2000; NREL/SR-570-27613.

[7] Wan X H, Chen H P, Luo K, Yang H P, Zhang S H. Methods to improve the stability of bio-oil, Chemical Industry and Engineering Progress, 2006; 25: 765－769.

[8] Diebold J P, Czernik S. Additives to lower and stabilize the viscosity of pyrolysis oils during storage. Energy and Fuels, 1997; 11: 1081－1091.

[9] Scholze B. Long-term stability, catalytic upgrading, and application of pyrolysis oils- Improving the properties of a potential substitute for fossil fuels. Dissertation, 2002.

[10] Wu X W. Effects of different kinds of additives and storage methods on the stability of bio-oil. Master Degree thesis, 2011.

[11] Morris K M. Fast pyrolysis of bagasse to produce Bio-oil fuel for power generation. International Sugar Journal, 2001; 103: 259－263.

[12] Soltes E J, Li J-C K. Hydroprocessing of Biomass tars for Liquid engine Fuels. Progress in Biomass Conversion, 1984.

[13] Oasmaa A, Leppamaki E, Koponene P. Physical characterization of biomass-based pyrolysis liquid: application of standard fuel oil analyses, Technical Research Centre of Finland, VTT Publications, Espoo, Finland, 1997; 306.

[14] Chen T J, Deng C J, Liu R H. Effect of Selective condensation on the characterization of bio-oil from pine sawdust fast pyrolysis using a fluidized-bed reactor. Energy and Fuels, 2010; 24, 6616－6623.

[15] Oasmaa A, Kuoppala E, Solantausta Y. Fast Pyrolysis of Forestry Residue. 2. Physicochemical Composition of Product Liquid. Energy and Fuels, 2003; 17, 433－443.

[16] Shen C J, Liu R H, Chen T J. Influence of storage temperature on stability of physicochemical properties of sawdust pyrolysis bio-oil. Transactions of the CSAE, 2011; 27: 276－281.

[17] Czernik S, Johnson D K, Black S. Stability of wood fast pyrolysis oil. Biomass and Bioenergy, 1994; 7: 187－192.

[18] Wang H. An experimental study on determination of the water content in bio-oil by karl-fischer titration. Renewable Energy Resources, 2005; 3: 17－20.

[19] Oasmaa A, Kuoppala E, Selin J-F, Gust S, Solantausta Y. Fast Pyrolysis of Forestry Residue and Pine. 4. Improvement of the Product Quality by Solvent Addition. Energy and Fuels, 2004; 18: 1578－1583.

[20] Boucher M E, Chaala A, Roy C. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part I: Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase. Biomass and Bioenergy, 2000; 19: 337－350.

[21] Hilten R N, Das K C. Comparison of three accelerated aging procedures to assess bio-oil stability. Fuel, 2010; 89: 2741-2749.

[22] Liu R, Deng C, Wang J. Fast pyrolysis of corn straw for bio-oil production in a bench-scale fluidized bed reactor. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 2009; 32: 10.

[23] Putun A E, Ozcan A, Putun E. Pyrolysis of hazelnut shells in a fixed-bed tubular reactor: yields and structural analysis of bio-oil. Journal of Analytical and Applied Pyrolysis, 1999; 52: 33－49.

[24] Williams E A, Williams P T. Analysis of products derived from the fast pyrolysis of plastic waste. Journal of Analytical and Applied Pyrolysis, 1997, 40-41: 347－363.

[25] Ates F, Putun E, Putun A E. Fast pyrolysis of sesame stalk: yields and structural analysis of bio-oil. Journal of Analytical and Applied Pyrolysis, 2004; 71: 779－790.

[26] Mullen C A, Strahan G D, Boatent A A. Characterization of various fast-pyrolysis bio-oils by NMR spectroscopy. Energy an d Fuels, 2009; 23: 2707－2718.

[27] Wisniewski Jr A, Wiggers V R, Simionatto E L, Meier H F, Barros A A C, Madureira L A S. Biofuels from waste fish oil pyrolysis: Chemical composition. Fuel, 2010; 89: 563－568.

[28] Xu J M, Jiang J C, Sun Y J. Bio-oil upgrading by means of ethyl ester production in reactive distillation to remove water and to improve storage and fuel characteristics. Biomass and Bioenergy, 2008; 11: 1056－1061.

[29] Ben H, Ragauskas A J. In situ NMR characterization of pyrolysis oil during accelerated aging. Chem Sus Chem, 2012; 5, 1687－1693.

[30] Yu F, Deng S, Chen P, Liu Y, Wan Y, Olson A, et al. Physical and chemical properties of bio-oils from microwave pyrolysis of corn stover. Applied Biochemistry and Biotechnology, 2007; 137-140: 957－970.