Effect of Methanol Addition on Properties and Aging Reaction Mechanism of Bio-oil during Storage

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Abstract In order to improve storage stability of bio-oil from pine wood pyrolysis with fluidized bed reactor, methanol in different proportions (3wt.%, 6wt.%, 9wt.%, 12wt.% and 15wt.%) was added into bio-oil. The changes of physicochemical properties of bio-oil samples such as water content, pH value and viscosity and the aging reaction mechanism during 35 days storage were investigated. During the storage, polymerization reaction and aging reactions occurred in bio-oil samples and addition of methanol could delay the aging process of unimolecular elimination reaction. Phenols of methanol/bio-oil could react following three possible reaction mechanisms: guaiacols ortho-methoxyl substitution, S_N1 and S_N2 reaction of ortho-hydroxyl substitution of catechol.

Keywords: Fast pyrolysis bio-oil; methanol additive; physicochemical properties; aging reaction mechanism

1. Introduction

Pyrolysis bio-oil is a liquid product derived from biomass fast pyrolysis which has potential to replace fossil fuel [1]. Compared to fossil fuels, bio-oil containing a low quantity of sulphur and nitrogen, is considered as a clean and renewable energy which is easy to be transported[2]. The biomass resource is abundantly available. And bio-oil can contribute to reducing the greenhouse effect by reducing CO_2 emissions. However, the pyrolysis process is not thermally balanced so the fuel quality of bio-oil is inferior to that of conventional fuels and it is unsteady during storage. The viscosity and water content will be increased with storage time. As a consequence, delamination of bio-oil will take place at last. Such disadvantages act as a barrier to large-scale applications of bio-oil.

According to recent studies [3, 4], the quality of bio-oil is influenced by material types and production technology. The cause of poor stability is ageing-related reactions and reactions among compounds, such as esterification, etherification and polymerization and alcoholization. These reactions will enlarge polar differences among the bio-oil components and cause the formation of larger molecules, ultimately resulting in phase separation and increases in viscosity.

There are several methods of improving the stability of bio-oil [5-7]. Considering the simplicity, solvent addition is a relatively easy, economic and practical approach to improve some undesired properties of bio-oils, which has beneficial effects on the oil properties for bio-oil quality upgrading [8-10].

Diebold et al. [11] showed an alternative method of adding several kinds of solvent into the pyrolysis oil inluidng additives (10wt.% ethyl acetate; 5wt.% methyl isobutyl ketone and 5wt.%

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methanol; 10wt.% ethanol; 5wt.% methanol and 5wt.% methanol; 10wt.% acetone; and 10wt.% methanol) to stabilize the viscosity of bio-crude. Methanol was found to be one of the best additive. Scholze [12] diluted the bio-oil with 20 wt.% methanol to stabilize the viscosity of bio-crude. The average molecular weight of the treated bio-oil was decreased. Accordingly, it is a good way to improve the stability of bio-oil by adding solvents, but how solvents influence the physicochemical properties of bio-oil is not revealed or detailed.

Adding solvent into bio-oil may reduce the reaction rate, lower its viscosity and improve its stability, which is considered as an effective way to upgrade the bio-oil [8, 13]. But the possible reaction mechanism of pyrolysis bio-oil with methanol during the storage 35 days has not been paid much more attention to.

Based on the previous studies [14-17], the objectives of this research were to add methanol at different mass concentrations into bio-oil to investigate its effect on its physicochemical properties during storage, and to find out tentative mechanistic pathways of chemical reactions during the aging process of pyrolysis bio-oil with methanol in 35 days storage.

2. Materials and methods

2.1. Bio-oil production

The bio-oil was produced from the fast pyrolysis of pinewood in a continuously fed bubbling fluidized bed reactor. The pyrolysis temperature was 500 °C and the fluidizing gas was nitrogen with a fluidization gas flow rate of 60 L/min. The bio-oil collection system was comprised of multistage condensers and electrostatic trap. Prior to commencing the pyrolysis processing, the sawdust was milled (30-80 mesh) and dried for 24 h at 105 °C. After production, the bio-oil was sealed in glass bottles and temporarily stored in a freezer at 4 °C before further use.

Elemental analysis of carbon, hydrogen and nitrogen was performed using the Vario EL element analyser. The results obtained from the elemental analysis of sawdust (air dry basis) are shown in Table 1. The initial bio-oil was found to have a high heating value of 20.944 $MJ \cdot kg^{-1}$. Its density was 1.203 $g \cdot ml^{-1}$ and its ash content was 0.528%. The bio-oil appeared to be a dark brown and single-phase liquid with irritant smell. The bio-oil yield is showed in Table 2.

Table 1 Element analysis of pinewood (air dry basis, wt %)

Chemical element	C	H	N	O and others
Pinewood	48.42	5.51	0.3	45.77

Table 2 Bio-oil yield

Batch	Biomass mass /g	Bio-oil mass /g	Bio-oil yield /wt. %
1	1429	758	53.04
2	1307	694	53.10

2.2. Experimental procedure

Methanol was added into the bio-oil at different mass concentrations (3 wt.%, 6 wt.%, 9 wt.%, 12 wt.% and 15 wt.% respectively). The blended bio-oil was stored in small sealed glass vials with a volume of 50 mL at 25 °C for 35 days. Values such as water content, viscosity (25 °C) and pH

value (25 °C) were measured before storage and on the 0, 7th, 14th, 21st, 28th and 35th day, respectively.

2.3. Analysis methods

The water content of the bio-oil was measured according to Karl Fisher reagent-volumetric method (ASTM E203-08) using the moisture tester from Metrohm Instrument Co., Ltd., type KFT 870. The kinematic viscosity of the bio-oil was tested according to capillary method through viscometer (ASTM D445) using a petroleum product kinematic viscosity tester, type SYD-265H, from Shanghai Changji Geological Instrument Limited Company. The pH value of the bio-oil was determined by the pH-potentiometer method from Shanghai Leici Instrument Plant, type PHS-3CT by using a particular electrode for ion-poor media. The HHV was tested 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 density of the bio-oil was measured by digital density meter (ASTM D4052-11) method using density determination apparatus from Anton Paar Co., Ltd., type DMA 4100M. The ash content of the bio-oil was tested according to ASTM D482-2007 method using Ash Determination Apparatus from Shanghai Shenkai Petroleum Instrument Co., Ltd., type SYP1005-I. All of the measurements were repeated in quadruplicate and the experimental repetitive errors meet the requirements of the corresponding method. The average values are reported.

GC-MS analysis was used to identify chemical compounds of bio-oils. It contained an AutoSystem XL GC and TurboMass MS (Perkin Elmer, USA) with DB-1MS capillary column (0.25μm×0.25mm i.d.×30m). The column temperature was set to 40 °C and maintained for 10 min, and then increased to 250 °C at a heating rate of 5 °C/min. The detector temperature was 280 °C. Helium was applied as carrier gas and the flow rate was 1.2 mL/min.

FT-IR spectra were recorded on an EQUINOX 55 FT-IR spectrometer (Bruker Inc., Germany) in the transmission mode which operated at a setting of 32 scans by KBr smear. All spectra were tested from 4000 to 400 cm^{-1}. All FT-IR spectra were normalized after acquisition and processed with the OPUS software (Bruker Inc., Germany).

3. Results and discussion

3.1 Effect of adding methanol on the water content

Water content is an important indicator to evaluate the quality of bio-oil. In the previous study, Czernik [11, 18] et al. reported that the water concentration in the bio-oil increased first and then decreased with storage time. In this study, the water content showed the same tendency with storage time. Fig. 1 shows the water content of the bio-oil stored for 35 days.

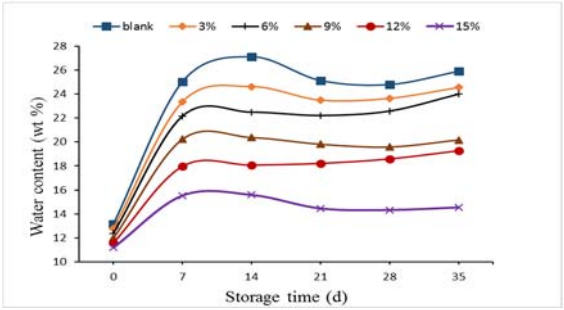

Fig. 1 Water content of the bio-oil stored for 35 days.

The result showed that the water content in crude bio-oil increased with storage time. According to Fig. 1, the water content was increased with the addition of methanol. Compared to the 0 day, the water content of the methanol-treated groups was increased by 105.85%，92.80%, 81.66%, 70.03%, 55.91% and 39.32%, respectively at the 14th day. The water content was reduced with the addition of methanol from the 14th day. Acting as an active reactant, methanol can react with the components in bio-oil [19]. It also can inhibit some aging-related reactions to delay moisture increase [8]. The reasons might be that water content was increased and more hydrogen ions were dissolved in the water [20]. This can be well proved by the moisture difference between the blank and the blended groups on the 14th day. Compared to the 14th day, the water content of the methanol-treated groups was decreased by 4.59, 1.24, 2.75, 0.08 and 7.25 %, respectively, at the 21st day. The presence of water contributed to the phase separation and greatly lowered its heating value [21]. So it is of great significance to lower the water content. Water content was steady for all groups from the 21st day to the 35th day. It was a prompt effect and was maintained to the end of storage. Fig. 2 shows the pH value of the bio-oil stored for 35 days and Fig.3 shows the viscosity (40°C) of the bio-oil stored for 35 days. Combined with the same variation of the pH value and the constantly increasing viscosity in Fig.2 and Fig.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 [8, 13]. The variation of water content in each methanol treated group was not exactly the same. The chemical reactions between the solvent and the bio-oil components occurred quickly for the prior 7 days, so the water content increased in each group. After 35 days storage, compared with the water content of 25.89wt.%, the 15% treatment group showed the lowest water content which was 14.55wt.% for the treated sample with 15wt.% methanol addition, respectively.

The effect of methanol additive was analyzed by the ANOVA two-way repeated-measures. The results showed that both the storage time and the additive concentration had significant influences on the water content. Interactions of the two factors also had significant influences at 0 day. Least significant difference (LSD) achieved 0.1073. According to the LSD of storage time and additive concentration, there were significant differences in water content on the other storage time among different methanol concentrations. T-test of storage time and additive concentration also indicated that there were significant differences in water content among the storage time. ANOVA analysis indicates that methanol had a certain effect on controlling water content.

3.2. Effect of adding methanol on the pH value

The pH value of the bio-oil became smaller with storage. Fig. 2 shows the pH value (25 °C) of the bio-oils stored for 35 days. It is shown that bio-oil had a pH value of between 2.20 and 3.26.

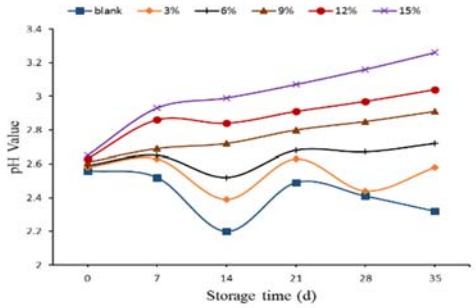

Fig. 2 pH value of the bio-oil stored for 35 days.

Fig. 2 shows that the pH value was an obvious improvement after adding methanol. This was a prompt effect and could maintain to the end of storage. Compared to the blank, the pH value of the treatment groups increased with methanol concentration by 0.78, 1.17, 1.95, 2.73 and 3.52%, respectively before storage. It shows that the pH value of the blank did not have an obvious change so much during storage. It can be found that each group changed differently with storage time. It may be the reason that the acidification tendency was not changed with the consumption of the methanol. When the methanol content was above 6.0 wt.%, pH value began to increase with the storage duration.It changed from 2.32 to 3.26 for the sample with 15 wt.% of methanol addition after 35 d storage.The difference between blank and 15 wt.% methanol treatment group was the largest, reaching 0.79. The pH value of blank was kept decreasing trend with storage time. As for methanol treatment groups, the pH value of each group was decreased to different extent with the similar acidification trend except the 21st day. The pH values of groups with methanol concentration of 3 wt.% and 6 wt.% were decreased by 0.24 and 0.13 at the 14th day, respectively. In the other treatment group, the pH value has been increased. It is supposed that solvent addition can impact the pH value by either two mechanisms [8, 22, 23]: the first is the neutral dilution effect of the additive and the second is that the activity of H^+ would be inhibited by the additive as the additive would change the acidity environment. From the 14th day to the 35th day, the pH value of treatment groups has shown growth trend. According to the literature, the pH value of the bio-oil is stable in the early stages of storage [8, 13]. It is also reported that there is a certain relationship between the pH value and the water content of bio-oil [3, 8]. For 3 wt.%, 6 wt.%, 9 wt.%, 12 wt.% and 15 wt.% methanol treatment group, the pH values were achieved from 2.39, 2.52, 2.72, 2.84 and 2.99 to 2.58, 2.72, 2.91, 3.04 and 3.26, respectively. This indicates that the stability of the bio-oil was improved. The effect does not last long and the bio-oil undergoes acidification afterward. In general, pH value reflects the concentration of H^+ in homogeneous solution. This contributes to the acid environment that many aging reactions such as esterification, etherification and polymerization are based in. It is of great significance to improve the pH value of the bio-oil.

The effect of methanol additive was analyzed by the ANOVA two-way repeated-measures. Table 3 shows significance test of influence of different concentration of methanol on pH at 25 °C of bio-oil. Table 4 shows least significant difference of pH at 25 °C of bio-oil at different time. The results showed that both the storage time and the additive concentration had significant influences on the pH value. Interactions of the two factors also had significant influences. According to the least significant difference (LSD) of storage time and additive concentration, there were significant

differences in the pH value between each period of different concentrations and between each concentration in different periods of time. ANOVA analysis demonstrates that methanol has a certain effect on preventing bio-oil acidification.

Table 3 Significance test of influence of different concentration of methanol on pH at 25 °C of bio-oil

	3%*	6%**	9%**	12%**	15%**
P>t	0.0214	0.0097	0.0097	0.0051	0.0052

* Significant, **very significant

Table 4 Least significant difference of pH at 25 °C of bio-oil at different time

	0d	7d	14d	21d	28d	35d
LSD	0.9875	0.1529	0.1921	0.1189	0.1008	0.0951

3.3. Effect of adding methanol on the viscosity

Larger molecules produced by aging reactions will cause an undesirable increase in viscosity [24, 25]. Fig. 3 shows the viscosity of the bio-oils stored for 35 days.

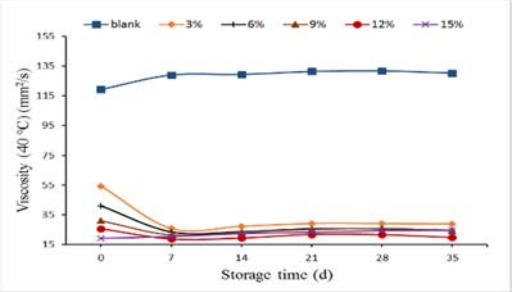

Fig. 3 Viscosity (40°C) of the bio-oils stored for 35 days.

According to Fig. 3, the viscosity decreased sharply with the addition of methanol. Compared to the blank, the initial viscosity in the treatment groups was significantly decreased by 54.24%, 65.45%, 73.91%, 78.35% and 83.73%, respectively, before storage, which is proportional to additive concentration. Each group showed a similar increasing trend with a relatively steady increasing rate before day 35. The increasing rates of treatment groups were 29.025, 24.616, 24.407, 19.852 and 24.704 mm^2/s, respectively, which were improved compared with that of the blank 30.075 mm^2/s. After storage, the treatment groups decreased by 46.76, 40.19, 21.47, 23.04 and 27.42%, respectively. The variation of viscosity was caused by the change of the average molecular weight [11]. Adding methanol can not only decrease the initial viscosity but also decrease its increasing ratio. This is achieved through three main mechanisms: physical dilution, lowering the reaction rate or by changing the oil microstructure and reacting with the components to stop further chain growth [4, 22].

The viscosity of the methanol/bio-oil samples was obviously lower than that of the raw bio-oil, which indicated that methanol could effectively inhibit the viscosity growth and reduce viscosity greatly during storage. It is postulated that methanol addition has impact on the bio-oil viscosity by four mechanisms [4, 9, 22]: (1) physical dilution will affect the inner chemical reaction; (2) reducing

the reaction rate by molecular dilution; (3) methanol addition will change the bio-oil microstructure; (4) reactions between the solvent and the bio-oil can prevent further inner chain growth. The fact that the initial viscosity decreased dramatically well proved the first mechanism. Smaller decreasing rates shown in treatment groups illustrated the second and third mechanisms.

The effect of methanol additive was analyzed by the ANOVA two-way repeated-measures. The results showed that both storage time and additive concentration had significant influences on the viscosity. Interactions of the two factors also had significant influences. According to the LSD of storage time and additive concentration, there were significant differences in viscosity between each period of time of different concentrations and between each concentration in each period of time. ANOVA analysis demonstrates that methanol had a significant effect on improving bio-oil viscosity.

3.4. GC-MS analysis

The information of bio-oils components was obtained from GC-MS analysis. Since there was too many components in bio-oil, the components with relatively high percentage were picked out and were classified by phenols, ketones, acids and furans. Fig. 4 shows relative peak area percentage distribution of component groups in bio-oil samples with different content of methanol. Since the percentage changes of component groups were the result of the chemical reaction during storage, some chemical reactions were summarized and speculated by these changes.

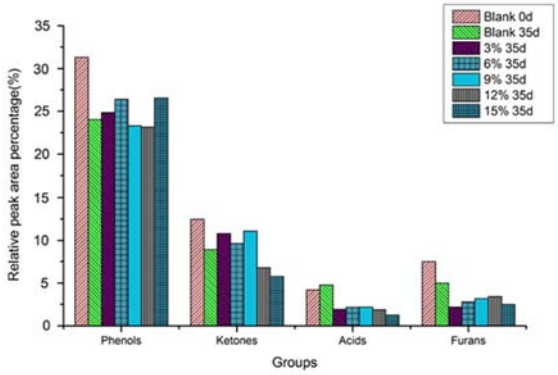

Fig. 4 Relative peak area percentage distribution of main component groups in bio-oil samples with different content of methanol

From Fig. 4, it can be seen that without methanol, the content of phenols was decreased from 31.3% to 24.1% during storage. The reason of phenols decrease might be the reaction of phenols with aldehydes to produce polymers [26]. The phenols contents of bio-oil samples after storage were changed to 24.1%, 24.8%, 26.0%, 23.3%, 22.7% and 26.6% when the methanol addition changed from 0% to 15%. The addition of methanol increased the phenols contents by 3.0%, 7.9%, -3.3%, -5.8% and 10.4%, respectively. Generally, the content of phenols of samples with methanol has an increased trend. It showed that the methanol addition could prevent the reaction of phenols.

It can be seen that after storage, the contents of ketones of bio-oil samples without methanol were decreased from 12.4% to 8.9%. And the contents of ketones of samples with 3 wt. %, 6 wt. %, 9 wt.%, 12 wt.%, 15 wt.% methanol were 10.8%, 9.6%, 11.1%, 6.8% and 5.8%, respectively. Compared with the blank sample which was stored 35 days, the contents increased by 21.3%, 7.9%, 24.7%, -23.6% and 34.8%, respectively. The hydration of ketones with water might be the reason

of ketones decreasing [4]. But in the low methanol content (under 12 wt. %), the extent of decreasing was lower than the sample stored for 35 days without addition. By contrast, the contents of ketones with high methanol (above 12 wt. %) was much lower than without addition stored for 35 days. According to Fig. 4, the addition of methanol with high concentration accelerated the decrease of ketones but the addition of methanol with low concentration could delay the decrease. It could show that low concentration of methanol was more conducive to extend the aging process.

The content of acids was increased from 4.2% to 4.8% after storage in the blank group, which was increased by 12.5%. But the addition of methanol greatly reduced it. The contents of acids changed from 4.8% to 1.3% when the methanol addition increased. It was decreased by 60.4% of 3 wt.% methanol bio-oil, 52.4% of 6 wt.% and 52.4% of 9 wt.% methanol bio-oil, 60.4% of 12 wt.% methanol bio-oil, 72.9% of 15 wt.% methanol bio-oil, respectively. The reason for the decrease of acids was due to the esterification of organic acids with alcohols[4]. The increased content of acids was related with the process of bio-oil aging, and the function of methanol could reduce the acids efficiently. But the difference between various concentrations of methanol was not significant for bio-oil stability

From Fig. 4, it could be illustrated that a decreased content of furans of bio-oil samples without methanol from 7.5% (before storage) to 5.0% (after storage) was observed, which reduced by 33.3%. The hydration of phenols or ketones functional group in furans with water might be the reason of the decrease[4]. When methanol was added into bio-oil, the content of furans decreased more than the blank one after storage. The contents of furans of samples were 2.2% (3 wt.% methanol), 2.8% (6 wt.% methanol), 3.2% (9 wt.% methanol), 3.4% (12 wt.% methanol) and 2.5% (15 wt.% methanol). It decreased by 56.0%, 44.0%, 36.0%, 32.0% and 50.0%, respectively. It implied that the addition of methanol enhanced the reaction of hydration of phenols or ketones.

Fig.5 shows the relative peak area percentage distribution of six components with high percentage of all samples. Fig.5 showed content of phenols including acetovanillone, 4-Ethyl-2-Methoxyphenol, phenol and pyrocatechol was changed. It was indicated that the contents of pyrocatechol, 4-ethyl-2-methoxyphenol and acetovanillone of the bio-oil sample without methanol were decreased after 35 days storage. Compared with blank groups, the contents of the three components were increased when methanol was added into bio-oil before storage, especially pyrocatechol. It was shown that the content change of pyrocatechol, 4-ethyl-2-methoxyphenol and acetovanillone might be the main reason of the content change of phenols. The content of 5-methyl-2-furfural, which is a kind of furans, was decreased after storage in the blank group and the contents of 5-methyl-2-furfural of bio-oil samples with methanol were lower than blank groups. The contents change of furans might be the result of the content change of 5-methyl-2-furfural. Meanwhile, it was shown that the content change of ethyl-2-oxo propanoate (belongs to the product of acids condensation reaction) was similar to the change of acids. It might be the main reason for the change of acids contents.

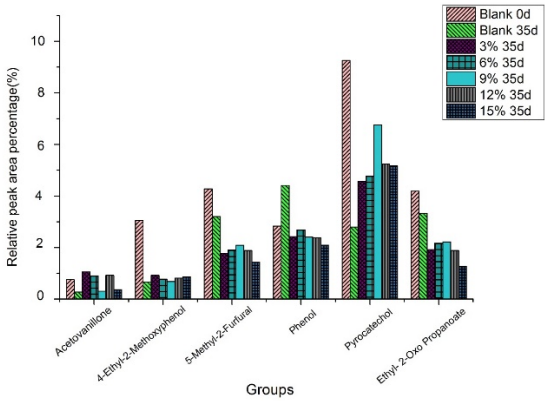

Fig.5 Relative peak area percentage distribution of six components in bio-oil samples with different content of methanol.

3.5. FT-IR analysis

In order to study bio-oil functional group changes, FT-IR analysis was utilized to investigate the chemical structure changes of bio-oil with different content of methanol in storage. Table 5 shows the evaluation and assignment of the FT-IR spectra functional group of bio-oil.

Table 5 Evaluation and assignment of the FT-IR spectra functional group of bio-oil

Absorbance frequency(cm^{-1})	Assignment of functional groups
3382-3439	O-H stretching vibration of the hydroxyl groups H_2O broad. absorbance: hydrogen bond effect in the present of water, alcohols, organic acids, etc.
2963	Symmetric and asymmetric stretching vibration of the aliphatic -CH_2 group.
2930	Symmetric and asymmetric stretching vibration shoulder of the aliphatic -CH_3 group.
1723	C=O stretching vibration in unconjugated ketones, carboxylic acids, carbonyl and ester groups.
1650	C=O stretching vibration of carbonyl groups in conjugated p-substituted aryl ketones, hydroxyl unsaturated ketones,
1611	Aromatic C=C ring breathing, aromatic C=C skeletal vibrations, C-O stretching vibrations.
1511	Aromatic ring vibrations, aromatics with various types of substitution.
1455	Bending vibrations of the CH_2 and CH_3 aliphatic groups.
1371	Symmetric deformation of C-H in methyl groups
1275	Vibrations of guaiacyl rings and stretching vibrations of C-O bonds.
1216-1236	C-C, C-O, and C=O stretching vibrations.
1127	C-O stretching vibration.
1048	Deformation vibrations of C-H bonds in aromatic rings.
888	Out-of-plane deformation vibration of C-H of terminal olefins.

817, 751	Vibrations of C-H bonds in syringyl units.
605	C-H bending vibration

Different adsorption peaks indicated different components in bio-oil samples. The broad O-H stretching vibrations between 3439-3382 cm^{-1} indicated the presence of water, alcohols, phenols, organic acids and other hydroxyl groups. For Blank 35 days bio-oil, the largest FT-IR transmission value was shown in 3384 cm^{-1}. Compared to the blank control group (Blank 0day and Blank 35 days bio-oil), the peaks of broad O-H stretching vibration of methanol addition group moved to higher wavenumber. It was shown that the component and structure of bio-oils were different between samples with different content of methanol and blank control group, and it was due to electron-withdrawing inductive effects of hydroxyl in methanol addition.

The stretching vibration at 2930 and 2963 cm^{-1} belonged to $-CH_2$ and $-CH_3$ groups. The peaks at 1371 cm^{-1} belonged to symmetric deformation of C-H in methyl groups. The $-CH_2$ and $-CH_3$ bending vibration peaks at 1455 cm^{-1} were indicated that long carbon chain existed in bio-oil samples. What is more, the peaks at 1371 cm^{-1} belonged to symmetric deformation of C-H in methyl groups.

Absorption peak located in about 1723 cm^{-1} contributed to carbonyl group, indicating the presence of carboxylic acids, carbonyl and ester groups. After storage, the peak which belonged to the carbonyl group of the bio-oil without methanol (Blank 35 days) in 1723 cm^{-1} was much higher than the bio-oil before storage (Blank 0d) and methanol addition group. It was indicated that C=O stretching vibrations including carboxylic acids, carbonyl and ester groups were consistent with saturated aliphatic esters [27]. It was indicated that acids, which is an intermediate product of esterification, were formed in aging reaction. Referred to the GC-MS analysis, acids as participants of esterification products, a proposed aging reaction, were identified in the aged oil. The reason might be that aging reaction had been taken place in Blank 35 days and methanol addition group could inhibit or delay the rate of aging reaction. During storage, the absorption peaks of the blank control group were increased in bands at 1723 cm^{-1}, 1649 cm^{-1} and 1611 cm^{-1}, which generally corresponded to decrease of the ratio of carbon content and oxygen content. This decrease could attribute to the formation of carbonyls including aldehydes, esters, and ketones [28]. The increased concentration of carbonyl, ester, and ether groups was characteristics of aging bio-oils as an effect of oxidation [29]. By contrast, the changes of these peaks and areas of methanol addition group were less obvious compared to original bio-oil (Blank 0d). It illustrated that methanol addition could prolong the storage time of original bio-oil.

There were some small weak bands around 1127 cm^{-1}. It represented C-O stretching vibrations for bio-oils resulting from methanol which was added to the bio-oil. Furthermore, the increased concentration of aromatic ring vibrations and C-H bonds in aromatic rings deformation vibrations was found from the peaks at 1511 cm^{-1} and 1048 cm^{-1}. The peaks location have changed, which indicated that during the storage, some reactions occurred in bio-oil samples and the addition of methanol had some effects on polymerization reaction and aging reactions.

The storage with different treatment also changed the intensity of some peaks of FT-IR spectra. There were obvious differences of intensity between different groups at the peaks of 3382 cm^{-1}, 1723 cm^{-1}, 1455 cm^{-1}, 1371 cm^{-1}, 1127 cm^{-1} and 1048 cm^{-1}. The strongest absorption peaks belonged to the blank one which was stored for 35 days. Some peaks of the samples with methanol addition had lower intensity than blank before storage. It indicated that the storage and methanol addition

changed the chemical component of the bio-oil samples and inhibited bio-oil aging proceeding.

4. Conclusions

(1) Methanol could decrease the initial water content of bio-oil. The more methanol was added, the less water content could be produced. However, more methanol could reduce the decreased tendency compared with blank.

(2) Methanol could improve the initial pH value of bio-oil. When the methanol content was above 6.0 wt.%, pH value began to increase with the storage duration and the effect was obvious. It changed from 2.32 to 3.26 for the sample with 15 wt.% of methanol addition after 35 d storage.

(3) Methanol dramatically decreased both the viscosity of initial bio-oil and the increasing the reaction rate of viscosity. The extent of decrease was related to the mass concentration of methanol.

(4) The content change of phenols in bio-oils was due to the difference of pyrocatechol, 4-ethyl-2-methoxyphenol and acetovanillone. The methanol function in aging bio-oil could decrease the content of furans, and the main reason of the contents change of furans was decrease of 5-methyl-2-furfural during the storage. Otherwise, the contents change of acids might be the result of condensation reaction of ethyl-2-oxo propanoate.

(5) Based on FT-IR analysis, the component and structure of bio-oils were changed. During the storage, some reactions occurred in bio-oil samples and the addition of methanol had some effects on polymerization reaction and aging reactions.

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Symbols used

Wavenumber	[cm^{-1}]	Unit of Fourier transform infrared spectroscopy
Heating rate	[5 °C/min]	Rate of heating per minute

Abbreviations

FT-IR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography-mass spectrometry
R-	Organic chemical function group

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