Research on Physical and Chemical Properties of Blended Bio-Oil Based on Fractionation

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To improve the properties of bio-oil, a new method was proposed that does not involve introduction of any energy medium. An ether-soluble fraction (ES), a dichloromethane soluble fraction (DCMS), and a dichloromethane insoluble fraction (DCMIS) of bio-oil were obtained using ether and dichloromethane as extraction solvents. The same amount of each fraction (10 g) was blended into bio-oil with a certain quantity of 100 g. The three samples were then placed in sealed vials and heated for 12, 60, and 180 h at both 60 °C and 80 °C in an oil bath. Based on the aging properties of the three fractions, blended bio-oil was prepared using ES and DCMS in certain volume ratio. The total yield of the three fractions combined was around 90 wt%; the weight loss was thought to be due to the volatilization of low molecular weight matter and water during the process of solvent evaporation using a rotary evaporator. The aging test results indicated that the DCMIS fraction had the poorest properties compared with ES and DCMS such as acid number, water content and viscosity. In order to get the best properties of blended bio-oil, the optimal volume ratio of ES/DCMS was 1/2 according to the aging test.

Keywords: Bio-oil; Aging; Fractions; Blended bio-oil

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INTRODUCTION

Currently, the wide use of conventional fossil fuels is causing a variety of economic and social problems, including depletion of natural resources, environmental pollution, and global warming. So it has become necessary to develop alternative, clean, and renewable energy resources to solve the above problems. There are various renewable resources available, such as wind, solar, hydrogen, nuclear, and biomass. Use of biomass as feedstock for energy and chemical production has attracted more and more attention in the last decade (Demirbaş 2000; Huber *et al.* 2006; Brunner 2009; Luo *et al.* 2010; Mazaheri *et al.* 2010).

Fast pyrolysis of biomass is one of the most promising technologies to utilize renewable biomass resources, which converts biomass into non-condensable gases, liquid oil, and charcoal. The potentially interesting second generation transportation fuel (fast pyrolysis oil) and bio-liquids derived chemicals can be produced through the fast pyrolysis process. Bio-oil derived from biomass is a complex mixture of hundreds of organic compounds, including alcohols, aldehydes, acids, esters, sugars, phenols, and their derivatives, named pyrolytic lignin (Bayerbach *et al.* 2006; Domine *et al.* 2008; Bayerbach and Meier 2009). Bio-oil is considered as a potential substitute for petroleum due to its outstanding characteristics of being both renewable and environmentally friendly (Garcia-Perez *et al.* 2007; Huber and Corma 2007; Mohan *et al.* 2006).

It is known that crude bio-oil is a low-grade liquid fuel that features several undesirable characteristics, such as high oxygen content, high acid number, *etc*. As such, bio-oil is unsuitable for direct use in internal combustion engines, and some refinement is needed. Various upgrading techniques, such as emulsification (Ikura *et al.* 2003), hydrotreatment (Pindoria *et al.* 1997; 1998; Zhang *et al.* 2005; Chiaramonti *et al.* 2007), catalytic cracking (Vitolo *et al.* 1999, 2001), adding solvent (Boucher *et al.* 2000; Scholze *et al.* 2001; Scholze and Meier 2001; Heeres *et al*. 2008), and steam reforming (Takanabe *et al.* 2004) have been reported.

In this paper, a new method of refinement is proposed to improve the properties of bio-oil without introducing any energy medium. After extracting the fraction which has the poorest properties, the rest of bio-oil could be potentially used as fuel. In the first step, an ether-soluble fraction (ES), a dichloromethane-soluble fraction (DCMS), and a dichloromethane insoluble fraction (DCMIS) of bio-oil are separated from each other using ether and dichloromethane as extraction solvents. In the second step, the same amount of each fraction (10 g) is added into 100 g of bio-oil; the three samples are then placed in sealed vials and heated in an oil bath for 12, 60, and 180 h at both 60 °C and 80 °C to discover which fraction had the poorest properties according to the aging test. The properties includes acid number, water content, viscosity and functional groups. In a third step, bio-oil is accordingly prepared with the other two fractions in different volume ratios. Finally, the optimal volume ratio of the two fractions is confirmed according to the aging test. After extracting the fraction which has the poorest properties, the rest of bio-oil could be potentially used as fuel.

EXPERIMENTAL

Materials

Bio-oil fractionation

The bio-oil sample used for experimental studies, using pine as feed stock, was provided by VTT, Finland. The solvents ether (CAS: 60-29-7) and dichloromethane (CAS: 75-09-2) were purchased from Aladdin Industrial Corporation, Shanghai, China. Crude bio-oil (100 mL) was put in a separatory funnel, and 200 mL of ether was added into the separatory funnel slowly. The separatory funnel was then shaken for several minutes and then allowed to rest for approximately 40 min. The solution separated into two layers. The upper layer and the bottom layer were designated the ether-soluble fraction (ES) and the ether-insoluble fraction (EIS), respectively. The ether was removed under reduced pressure with a rotary evaporator. Dichloromethane, 250 mL was added into the EIS, and the mixture was then shaken for several minutes before being left to sit for approximately 40 min. The mixture gradually separated into two layers. The bottom layer was designated as the dichloromethane-soluble faction of the EIS (DCMS) and the upper layer was the dichloromethane-insoluble fraction of EIS (DCMIS). The layers were separated and the dichloromethane was removed under reduced pressure with a rotary evaporator. The schedule of solvent extraction of bio-oil is shown in Fig. 1.

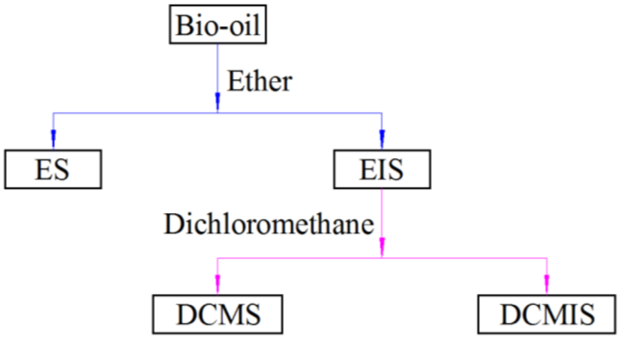

Fig. 1. The flowchart of solvent extraction of bio-oil

The ultimate analysis result was obtained on the basis of “as received” according to American Society for Testing and Materials (ASTM) D-5291 using a Carlo Erba Elemental Analyzer EA 1108 (Carlo-Erba, Milan, Italy). Table 1 gives the typical composition of crude bio-oil. The crude bio-oil had an elemental composition of 39.96 wt% C; 7.74 wt% H; 52.12 wt% O; 0.11 wt% N, and 0.07wt% S. The crude bio-oil had a high oxygen content, which contributed to high instability. Table 2 shows typical properties of crude bio-oil, indicating that crude bio-oil cannot be used as a suitable fuel compared to fossil fuels. For example, the water content in bio-oil is very high compared with petroleum (less than 1%), so that the bio-oil wasn't liable to be burning. The acid number in bio-oil was up to 79.23 mg KOH g^{-1}, while the value is usually less than 0.5 mg KOH g^{-1} in petroleum. The high acid number would cause the corrosion of equipment.

Table 1. Typical Composition of Crude Bio-Oil

Elemental analysis	Composition (wt %)
C	39.96
H	7.74
N	0.11
O	52.12
S	0.07

Table 2. Typical Properties of Crude Bio-Oil

Water content, wt%	28.05
Viscosity, (10^{-3} Pa·s)	67.39
Density, kg m^{-3}	1.20
Acid number, (mg KOH g^{-1})	79.23
HHV, MJ kg^{-1}	15.28
Solid content, wt%	0.18
Molecular weight	421

Aging test

To investigate the effect of each fraction on the stability of bio-oil and the synergistic effect of fractions during aging, an equal amount of each fraction was added into a certain amount of bio-oil. In order to keep the samples separate, the bio-oil solutions ES, DCMS, and DCMIS were defined as bio-oil-1, bio-oil-2, and bio-oil-3, respectively. The three bio-oil samples were then placed in sealed vials and heated for 12, 60, and 180 h at both 60 °C and 80 °C in an oil bath. After storage, visual inspection of the samples indicated whether any of the samples were coked.

Properties analysis

The acid number of the sample was determined using a Metrohm 728 stirrer (Metrohm, Switzerland), where 20 drops of each sample were dissolved in 50 mL of methanol for each measurement. The titrant was 0.1 N potassium hydroxide solution.

The water content of the sample was determined by Karl Fischer titration. Each sample was dissolved in methanol and titrated using Metrohm 794 Basic Titrino (Switzerland) and Karl Fischer volumetric reagent Aqualine Complete 5 (Sigma-Aldrich Co. Ltd). The water content test was repeated three times, and the average value was reported.

The viscosity of the sample was measured at 25 °C before and after storage at 60 °C and 80 °C using the Advanced Rheometer 2000 (TA Instruments, New Castle, Delware, US), with the shear rate of 100 s^{-1}. The measurements were repeated nine times to obtain the average value.

Fourier transform infrared spectroscopy (FTIR) were used to characterize the functional groups of the three blends. The attenuated total reflectance (ATR) method was used with a Varian 3100 FTIR (Varian, Inc. Palo Alto, Calif., US) spectrometer to record the spectra. The samples were applied as a film to the zinc selenide crystal. The resulting spectra were accumulated between 600 cm^{-1} and 4500 cm^{-1}.

RESULTS AND DISCUSSION

Yield of Three Fractions

Three sets of bio-oil fractionation experiments illustrated in “Materials section” were carried out to determine the yield of the three different fractions. The initial materials included: 10 g of bio-oil, 20 g of ether, and 15 g of dichloromethane. The results are shown in Table 3. The total yield of fractions was approximately 90 wt%. Some of the weight loss is assumed to be due to the evaporation of low molecular weight matter and water during use of the rotary evaporator.

Table 3. Yield of Three Fractions

Productions	Yield (wt %)		
	Batch 1	Batch 2	Batch 3
ES	41	38	37
DCMS	21	22	20
DCMIS	31	30	29
ES+ DCMS+ DCMIS	93	90	86

Properties of Bio-Oil Samples Before and After Aging

Acid number

The acid numbers of three bio-oil samples under different aging conditions are illustrated in Fig. 2. In general, acid number increased during the aging process, as illustrated by the three samples examined. Bio-oil-1 had the highest initial acid number, and the acid number increased slightly over time. The bio-oil-2 sample showed a trend in increasing the acid number similar to bio-oil-1. The initial acid number of bio-oil-3 was the lowest compared with the other two samples, but the increase in acid number was sharper than the bio-oil-1 or bio-oil-2. It can be concluded that the DCMIS fraction was more active than ES and DCMS, and the DCMIS generates more acid compounds during storage.

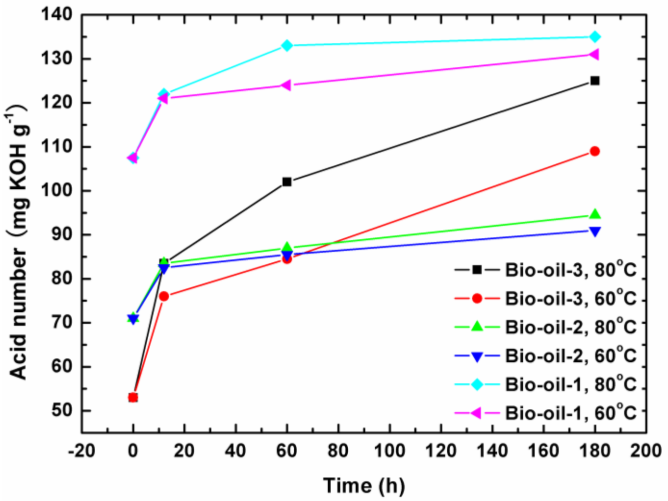

Fig. 2. Acid number of bio-oil samples stored under different conditions

Water content

The water content of three bio-oil samples under different aging conditions are shown in Fig. 3. The water content in bio-oil-3 was the highest before aging. Changes in water content during aging can be the result of competing mechanisms of hydration reactions (consuming water) and esterification and/or polycondensation reactions (producing water).

The water content of each bio-oil sample increased with time and temperature during aging. So it is concluded that the reactions producing water dominate hydration conditions. As shown in Fig. 3, the water content in bio-oil-3 increased by about 7%, which is higher than that in bio-oil-1 and bio-oil-2, and this shows increases in water content by about 2 to 3%.

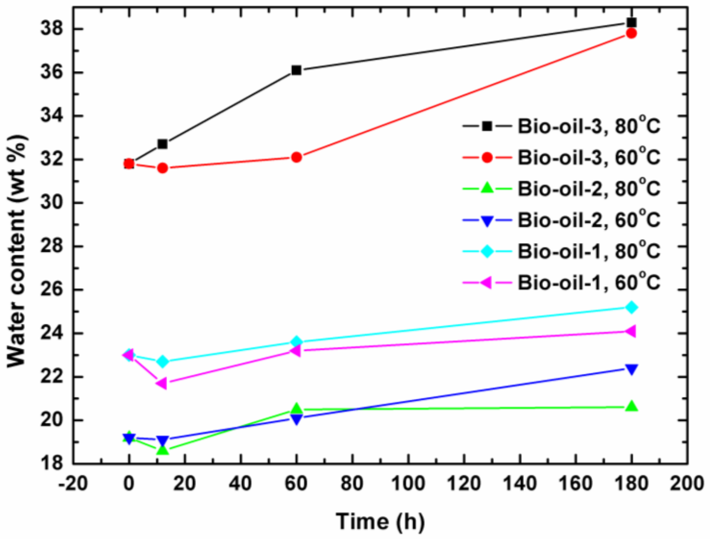

Fig. 3. Water content of bio-oil samples stored under different conditions

Viscosity

Figure 4 shows the viscosities of three bio-oil samples. The viscosity of the stored samples exhibited an overall downtrend within the first 12 h of aging. Just as illustrated in "water content", the water content decreased within the first 12 h. Normally, the water had the effect of decreasing the viscosity of samples. The probable reason was that some other small compounds were generated to dilute the bio-oil samples during storage, and this made the viscosity of bio-oil decrease, while the water content also decreased in this period. With the increase in time, the hydration reactions begin to dominate the aging pathway, making the samples exhibit a higher viscosity as water is absorbed by the system. Comparing the three bio-oils, the viscosity of bio-oil-3 exhibited the largest increase in viscosity. Moreover, a certain amount of char could be observed on the interior of the vial containing DCMIS.

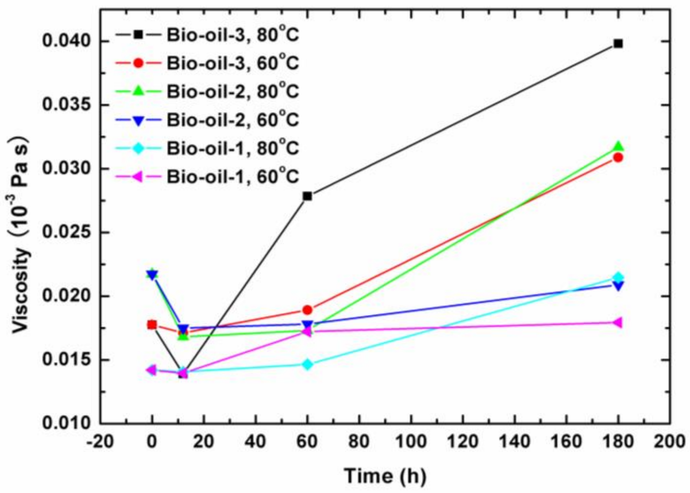

Fig. 4. Viscosity of bio-oil samples stored under different conditions

FTIR spectra

The chemical changes in the bio-oil samples resulting from storage can be observed in the FTIR spectra in Fig. 5. Because of the chemical complexity of bio-oil and its fractions, it is hard to get quantitative results from FTIR spectra. Therefore, the absorption intensity was used to contrast with each other. Absorption peaks exhibited in FTIR spectra of bio-oil samples in the absorbance at 1430 cm^{-1} and 3400 cm^{-1}were influenced by the aging process. No additional functional groups were generated during aging and only slight increase in absorbance was observed before 3000 cm^{-1}. The obvious growth in absorbance at 3400 cm^{-1} corresponds to O-H stretching in hydroxyl groups and the increase at 1430 cm^{-1} is ascribed to O-H bending vibration. The enhancement in absorbance here indicates the increase in water content of bio-oil, which was confirmed by the result obtained from Karl Fischer titration.

Based on above results, it is apparent that the DCMIS fraction had the least desirable properties compared with ES and DCMS during storage, which leads to negative effects associated with the usage of bio-oil. In order to use bio-oil effectively, the DCMIS fraction should be separated from bio-oil and an optimal ratio between the ES and DCMS should be found in order to prepare make-up bio-oil.

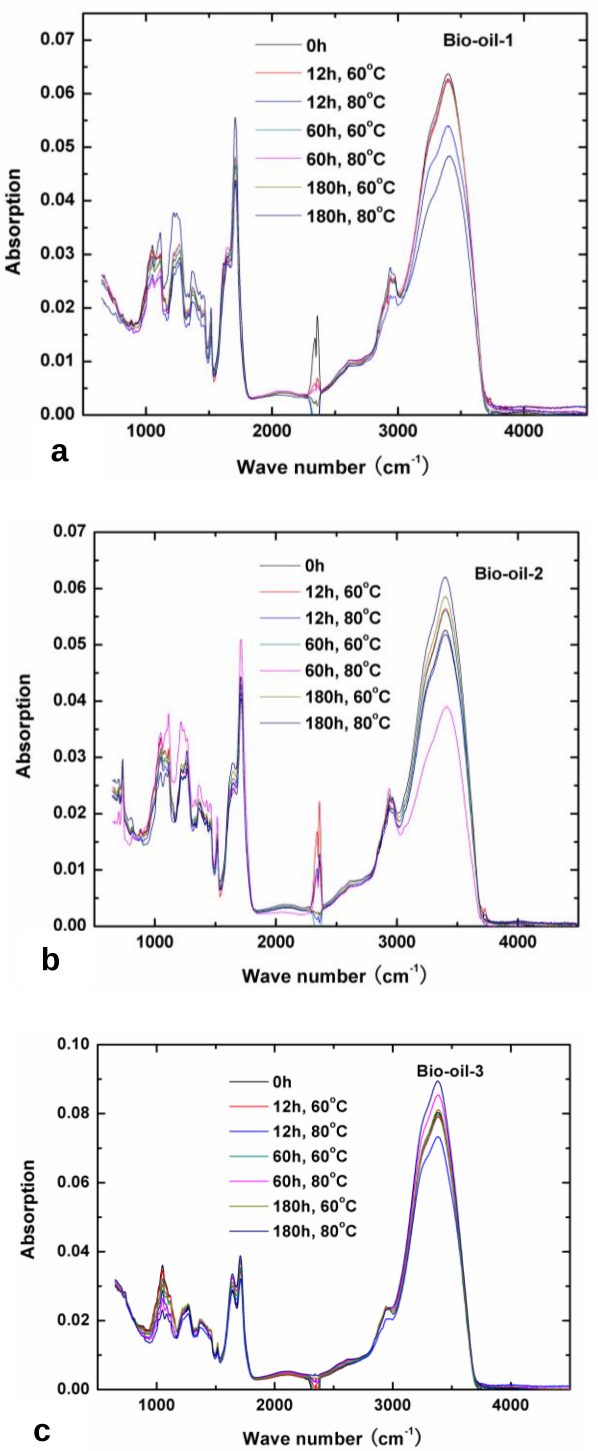

Fig. 5. FTIR spectra of bio-oil samples stored under different conditions. (a) Bio-oil-1, (b) Bio-oil-2, and (c) Bio-oil-3

Blended Bio-Oil Preparation and Aging Properties

In order to achieve the best properties of blended bio-oil during storage, the optimal volume ratio of ES/DCMS should be determined to prepare the blending bio-oil. A study of aging properties of different bio-oil fractions was undertaken. Three blended bio-oil samples using ES and DCMS with volume ratios of 1:1, 1:2, and 2:1 were prepared. The three samples were then placed in sealed vials and heated for 12, 60, and 180 h at both 60 °C and 80 °C in an oil bath. After storage, the water content, acid number, and functional groups changes were characterized, respectively.

Water content

Figure 6 illustrates the change in water content of blended bio-oil with different volume ratios of ES/DCMS under various aging conditions. The water content of the three samples increased with time. The optimal volume ratio of ES/DCMS was confirmed based on the growth rate of water content of the blended bio-oil stored for 180 h. As is shown in Table 4, the growth rate of water content was the lowest when the volume ratio of ES/DCMS was 1:2.

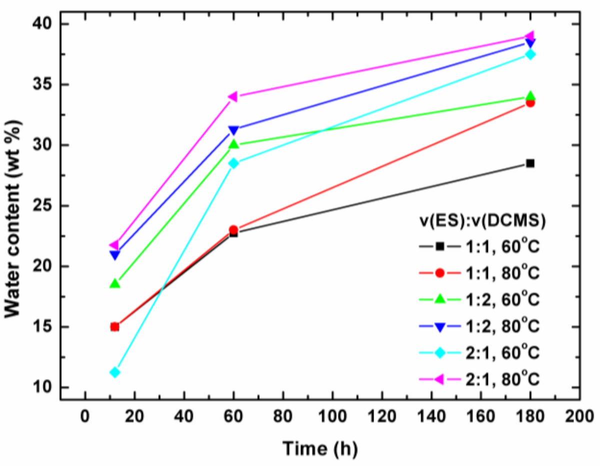

Fig. 6. Water content of ES/DCMS aged under different conditions

Table 4. Growth Rate of Water Content of ES/DCMS Aged for 180 h

Aging conditions	1:1; 60 °C	1:1; 80 °C	1:2; 60 °C	1:2; 80 °C	2:1; 60 °C	2:1; 80 °C
Growth rate	90.4%	123.3%	84.3%	85.9%	84.0%	230.9%

Acid number

Figure 7 illustrates the evolution of the acid numbers of three samples across differing storage periods.

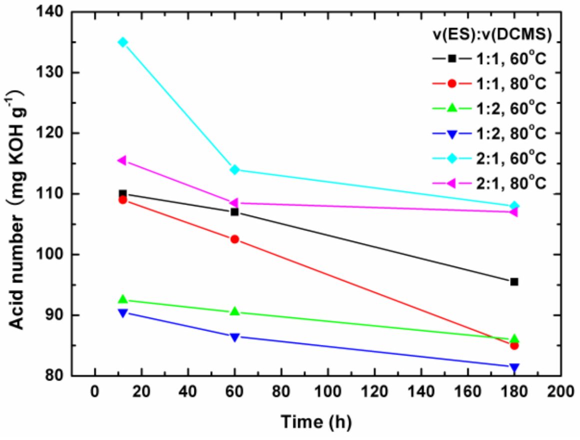

Fig. 7. Acid number of ES/DCMS aged at different conditions

It is apparent that the acid numbers decreased with storage time and temperature. The optimal volume ratio of ES/DCMS was confirmed based on the growth rate of acid number when stored for 180 h. As is shown in Table 5, the increase of the acid number was the lowest when the volume ratio of ES/DCMS was 1:2.

Table 5. Growth Rate of Acid Number of ES/DCMS Aged for 180 h

Aging conditions	1:1; 60 °C	1:1; 80 °C	1:2; 60 °C	1:2; 80 °C	2:1; 60 °C	2:1; 80 °C
Growth rate	13.6%	22.0%	7.5%	11.0%	6.9%	19.3%

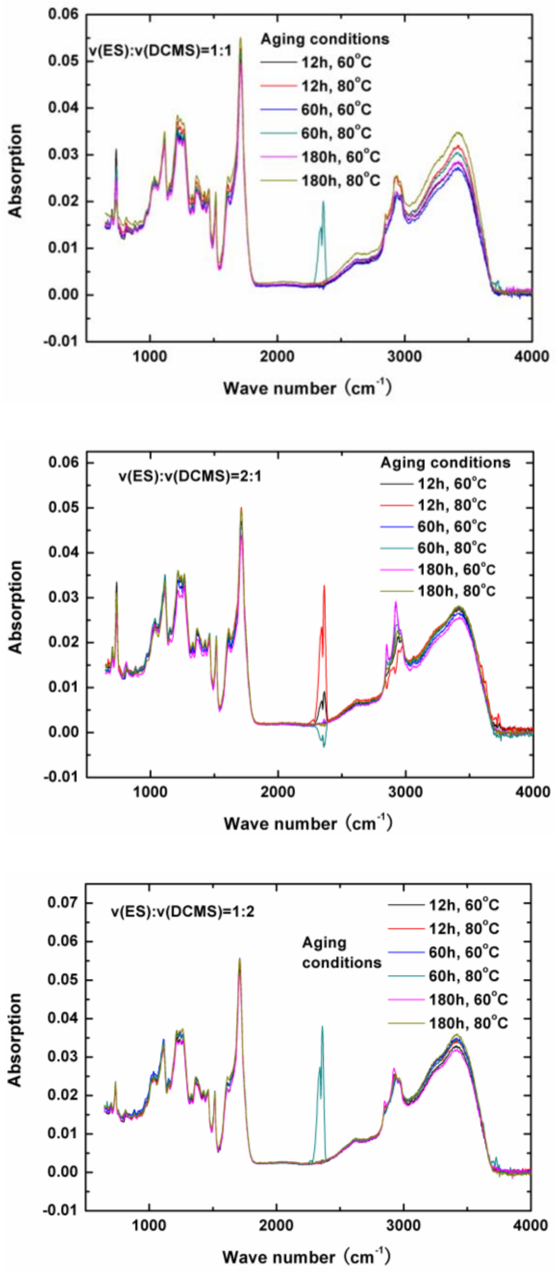

Fig. 8. FTIR spectra of ES/DCMS aged at different conditions

Functional groups

The functional group changes resulting from the storage of the samples can be observed in the FTIR spectra in Fig. 8. The increase in absorbance at 3400 cm^{-1} corresponds to O-H stretching in hydroxyl groups, and the increase at 1430 cm^{-1} corresponds to O-H bending vibration. The two peaks indicate the present of water in the samples. The slight increase in absorbance between 2850 and 3000 cm^{-1} corresponding to C-H stretching vibration indicates polymerization during storage. The absorbance at 1050 cm^{-1} (stretching of C-O-H) and 1200 cm^{-1} (stretching of C-O-C) suggest the formation of tertiary alcohols and phenols during aging. The increase in the carbonyl stretch at 1650 cm^{-1} (C=O) may be due to the formation of ester during storage.

The functional group changes were slight under different aging conditions. Furthermore, the absorption peaks matched well together when the volume ratio of ES/DCMS was 1:2 during various aging periods. This indicates that the make-up bio-oil was more stable when volume ratio of ES/DCMS was 1:2.

CONCLUSIONS

1. Three fractions of bio-oil were obtained using ether and dichloromethane and were described by the solubility of the products as ES, DCMS and DCMIS. The total yield of fractions was approximately 90 wt%. The weight loss was attributed to the evaporation of low molecular weight organic compounds and water during the process of solvent evaporation using a rotary evaporator.
2. The aging test showed that the DCMIS fraction was more active than ES and DCMS, and the DCMIS generated more acid compounds during storage; the water content in bio-oil-3 increased by about 7%, which was higher than that in bio-oil-1 and bio-oil-2. Comparing the three bio-oils, the viscosity of bio-oil-3 exhibited the largest increase in viscosity. Moreover, a certain amount of char could be observed on the interior of the vial containing DCMIS.
3. The blended bio-oil was prepared using ES and DCMS under various volume ratios. In order to get the best properties of blending bio-oil, the optimal volume ratio of ES/DCMS was 1:2 according to the aging test.

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