Physical and Chemical Properties of Bio-Oils From Microwave Pyrolysis of Corn Stover

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Abstract

This study was aimed to understand the physical and chemical properties of pyrolytic bio-oils produced from microwave pyrolysis of corn stover regarding their potential use as gas turbine and home heating fuels. The ash content, solids content, pH, heating value, minerals, elemental ratio, moisture content, and viscosity of the bio-oils were determined. The water content was approx 15.2 wt%, solids content 0.22 wt%, alkali metal content 12 parts per million, dynamic viscosity 185 mPa·s at 40°C, and gross high heating value 17.5 MJ/kg for a typical bio-oil produced. Our aging tests showed that the viscosity and water content increased and phase separation occurred during the storage at different temperatures. Adding methanol and/or ethanol to the bio-oils reduced the viscosity and slowed down the increase in viscosity and water content during the storage. Blending of methanol or ethanol with the bio-oils may be a simple and cost-effective approach to making the pyrolytic bio-oils into a stable gas turbine or home heating fuels.

Index Entries: Aging; chemical behavior; microwave pyrolysis; physical behavior; stability; bio-oils.

Introduction

It is imperative to find/develop alternative renewable fuels to address issues arising from rapid consumption of petroleum oils and rising interest in environment protection *(1)*. Generally, the energy generated by direct combustion has a maximum efficiency of more than 30%. It is believed that burning bio-oils produced from the thermochemical conversion of biomass is more efficient *(2)*. Bio-oils with little upgrading treatments are already suitable for turbine fuel and home heating oil uses, and therefore receiving much attention. Solantausta et al. *(3)* tested bio-oils produced

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from wood in a gas turbine, and concluded that the technical limitations to the use of the bio-oils in turbines could be minimized by optimizing their physical and chemical properties such as ash content, alkali content, heating value, and viscosity and modifying the gas turbine engine system. The ash present in the bio-oils reduces the protective oxide surface film of the engine *(4)*. Alkali metal sulfates and chlorides can accelerate the oxidation process *(5)*. The heating value of bio-oil is lower than for fossil fuel, and a significant portion of the bio-oil consists of water. The spray pattern and droplet size are influenced by fuel viscosity, which may be connected to the pressure drop in the fuel system lines because of high viscosity. Higher viscosities result in higher line pressure drops, requiring the fuel pump to work harder to maintain a constant fuel flow rate. Fuel viscosity also influences the performance of the fuel system control unit. Therefore, the bio-oils must be properly produced and/or improved in order to meet the gas turbine fuel specifications *(6)*.

This study was aimed at characterizing the physical and chemical properties of the bio-oils produced from a novel microwave pyrolysis process. The understanding of their physical and chemical behaviors is important to the design and control of processing parameters, product specifications, and product storage and transportation. Blending bio-oils with combustible solvents such as methanol and ethanol is a practical approach to the improvement of the bio-oil shelf stability and performance. It has been reported that the presence of methanol or ethanol in the bio-oil provides a simple method for controlling the viscosity of the bio-oil *(7)*, facilitating combustion, improving homogeneity, and enhancing stability *(8)*. Therefore, the effect of methanol and ethanol blending on the viscosity and stability of the bio-oils were also studied.

Materials and Methods

Materials

Corn stover (provided by Agricultural Utilization Research Institute, Waseca, Minnesota) used in this experiment was dried in air and pulverized mechanically and sifted through a 2 mm sieve before pyrolysis. The properties of corn stover are given in Table 1 and minerals in Table 2.

Apparatus and Process

Pyrolysis of corn stover was carried out in a microwave cavity oven by placing 150.0 g samples in a 1-L quartz flask, which in turn was placed inside the microwave cavity. The oven was purged with nitrogen gas at a flow rate of 200 mL/min for 2 min before microwave treatment to create an oxygen-free gas background. A constant power input of 600 W at 2450 MHz was supplied to the microwave oven. Heating of the corn stover last about 40 min, which is thought to be sufficient to allow complete pyrolysis according to preliminary experiments. The volatile pyrolyzates were condensed after passing through a water-cooling column and collected in a

Table 1
Properties of Corn Stover

Properties	Corn stover
Bulk density, at 20°C (kg/m^3)	557.0
Volatile matter	79.44
Fixed carbon	8.34
Moisture	7.66
Ash	5.75
Elemental composition (wt%)	
Carbon	40.35
Hydrogen	5.31
Nitrogen	1.12
Sulfur	0.09
Oxygen (by difference)	53.13
Gross heating value (MJ/kg)	24.5

bottle. This pyrolytic liquid is called bio-oil. The condensates adhering to the interior wall of the quartz flask were washed with ethanol into the pyrolytic liquid collection bottle. All liquid collected was concentrated at 40°C using a rotovap (Buchi R-141, Flawil, Switzerland) to a constant weight, and the weight recorded. All experiments and analyses were performed in triplicate with an experimental error ≤ ±1.0%.

Determination of Physical and Chemical Properties of Bio-Oils

The ash content of the bio-oils was determined following the procedure outlined in ASTM D 482-80 for petroleum products. The solids content was determined as ethanol insoluble material by Millipore (No. 4, Whatman) Filtration method. The pH of the bio-oils was observed using a digital pH meter (Accumet model 8250, Fisher Scientific, Fair Lawn, NJ). The minerals in the bio-oils were analyzed using the Inductive Coupled Plasma-Atomic Emission Spectrometer (ARL 3560, Waltham, MA). The heating value was measured as calorimetric value (higher heating value) by a Parr 1341 Oxygen Bomb Calorimeter (Parr Instrument Co., Moline, IL). The elemental ratio (C/H/N/O/S) of the samples was analyzed using an elemental analyzer (Leco 600, St. Joseph, MI). Water in the bio-oils was determined using a Karl Fischer titrator (Schott, Mainz, Germany; ASTM D 1744). The dynamic viscosity of oils was determined with a rotational viscometer (Brookfield DV-E, Middleboro, MA; ASTM D 445). The Brookfield rotational viscometer is equipped with a cover for preventing the evaporation of volatiles. The kinematic viscosity of the bio-oils was calculated by the dynamic viscosity divided by the density. Measurements for samples were taken at 22°C.

The homogeneity of the samples was determined using following procedure: 500 mL sample was pumped using a peristaltic pump (MASTERFLEX 07518-10, Vernon Hills, IL) at room temperature from bottom to

Table 2
Minerals of Corn Stover and Bio-Oils by ICP Analysis

Mineral (ppm)	Al	B	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	Zn
Corn stover	112.740	4.442	2389.500	0.120	0.506	3.530	149.880	10643	1642.800	23.082	15.049	4.440	429.820	1.680	40.417
Bio-oils	4.9215	2.848	6.833	0.0585	0.307	0.3965	7.589	3.127	1.8575	0.034	1.8155	0.953	1.5175	0.8215	0.7915

Table 3
Physico-Chemical Properties of Bio-Oils

Properties	Units	Bio-oil	Conventional bio-oils
pH		2.87	2.0–3.8
Moisture	wt%	15.2	15–30
Density at 20°C	g/mL	1.25	1.1–1.4
Dynamic viscosity at	mPa·s		
20°C		1270	–
40°C		185	–
50°C		60	–
80°C		34	–
Gross heating value	MJ/kg	17.51	15–19
Elemental composition	wt%		
C		60.66	55.3–63.5
H		7.70	5.2–7.0
N		2.02	0.07–0.39
S		0.15	0.00–0.05
Ash content	wt%	0.04	0.03–0.30
Solids content	wt%	0.22	<1

top for about 1 h per test. Samples were taken from the homogenized sample by pouring from the hose at the outlet of the pump. Microscope (×300 magnification) was used to capture the digitalized microscopic images of sample. The stability was determined using following procedure: 100 mL pyrolytic oils were placed in 150-mL amber bottles and stored at room temperature (22°C) or at elevated temperatures (40 or 60°C) in ovens over various time periods (30–60 d). After the designated time the samples were cooled rapidly and viscosity and water content were tested according to the methods described above.

Results and Discussion

The bio-oils from our process are dark brown viscous liquid. Some key physical and chemical properties of the oils are described in Table 3. As can be seen, these properties were in the range of bio-oils from other pyrolysis processes but significantly different from those of petroleum derived diesels.

Ash Content

The presence of ash in the bio-oil can cause erosion, corrosion, and gumming problems in the engine valves. The ash content of the bio-oils from microwave pyrolysis is 0.04 wt%. Problems associated with ash content become more serious when the ash content of the fuel is greater than 0.1 wt% *(9)*.

Solids Content

The solids content of bio-fuel from our microwave pyrolysis is 0.22 wt%. It lies in the lower range of the solids content of other bio-fuels reported in the literature (Table 3). Depending on their size, solid particles can wear the fuel system, block the filter, and clog the fuel nozzle *(6)*. Thereby the solids content is important with respect to the particulate emissions during the combustion process. The larger and the more the particles, the more serious the solids content problem is.

pH

The pH value of bio-oils from our microwave pyrolysis is 2.87. Most bio-oils have a pH in the range of 2.0–3.8 because of the presence of organic acids, mostly acetic and formic acid *(5)*. The acids in the bio-oils are corrosive to common construction materials such as carbon steel and aluminum, especially with elevated temperature and with the increase in water content. However, bio-oils are noncorrosive to stainless steels.

Mineral Contents

The presence of superscale magnesium, calcium, and alkali metals in a fuel used for gas turbine is rather troublesome. The melting of metals and the condensation of metal oxides can cause accelerated corrosion and erosion of turbine blades *(10)*. Furthermore, sodium and potassium are responsible for high-temperature corrosion whereas magnesium and calcium are accountable for hard deposition. The metal limits for a gas turbine fuel are 1 ppm for sodium and potassium, 0.5 ppm for calcium, and 0.5 ppm for vanadium. The main source of minerals in the pyrolytic oils is the char residues carried by the pyrolytic vapors. The metal contents of the bio-oils were found to be: 3 ppm K, 2 ppm Na, and 7 ppm Ca (Table 2). They are lower than those of the bio-oils generated by other processes. The alkali metal and calcium concentration in bio-oils can be reduced by the organic solvent dilution, which is a simple and cost-effective method to improve the fuel quality.

Heating Value

Bio-oils have a lower gross heating value than petroleum fuels and will therefore require an increased fuel flow to compensate the combustion in a firebox *(9)*. The gross heating value of our raw bio-oil sample is 17.51 MJ/kg (Table 3). It is similar as the gross heating values of bio-oils produced by other processes (15–19 MJ/kg) but lower than that of petroleum fuels (42 MJ/kg). The heating value of the bio-oils from microwave pyrolysis is approx 41.7% of a petroleum fuel oil. In other words, 2.4 kg of our bio-oil is required to provide the same energy as 1.0 kg of petroleum oil.

Table 4
High Heating Value of Bio-Oils and Bio-Oils With Solvent Addition

Samples	High heating value (MJ/kg)
Bio-oils	17.51
Aqueous phase	1.2
Bio-oils with 10 wt% methanol	16.21
Bio-oils with 20 wt% methanol	15.96
Bio-oils with 30 wt% methanol	13.47
Bio-oils with 10 wt% ethanol	14.15
Bio-oils with 20 wt% ethanol	12.07
Bio-oils with 30 wt% ethanol	11.98

The aqueous phase of pyrolytic liquid, methanol, and ethanol can be used as solvent to keep the bio-oils homogenous and low in viscosity. If the aqueous phase of pyrolytic liquid, methanol, and ethanol are to be blended into the bio-oils, it is important to determine the variations in the heating values of the blends. The gross heating value of the aqueous phase is 1.2 MJ/kg (Table 4), lower than that of the bio-oils. Methanol and ethanol also have lower energy density than the bio-oils. Therefore, the heating values of the blends are expected to be lower than that of the bio-oils.

Water Content

The water content in the bio-oils from our microwave pyrolysis of corn stove is 15.2% (Table 3). The water likely came from two sources: the moisture in the raw corn stover and the water produced as a result of the dehydration reactions occurring during the pyrolysis. Therefore, water content can vary in a wide range (15–30%) depending on the feedstock and process conditions *(11)*. At this concentration water is usually miscible with the oligo-cellulosic derived components because of the solubilizing effect of other polar hydrophilic compounds (low-molecular-weight acids, alcohols, hydroxyaldehydes, and ketones) mostly originating from the decomposition of carbohydrates. The presence of water has both negative and positive effects on the oil properties. Obviously, it lowers its heating value, contributes to the increase in ignition delay, and the decrease in combustion rate compared with engine fuels. On the other hand, it improves bio-oil flow characteristics (reduces the oil viscosity), which is beneficial to combustion.

Viscosity

In order to be considered as a gas turbine fuel, the bio-oils must meet certain viscosity standard. The viscosity of gas turbine oils is usually around 2.5–30 mm^2/s at 40°C *(7)*. The kinematic viscosity of the bio-oils was difficult to determine because the level of the bio-oils in the viscometer
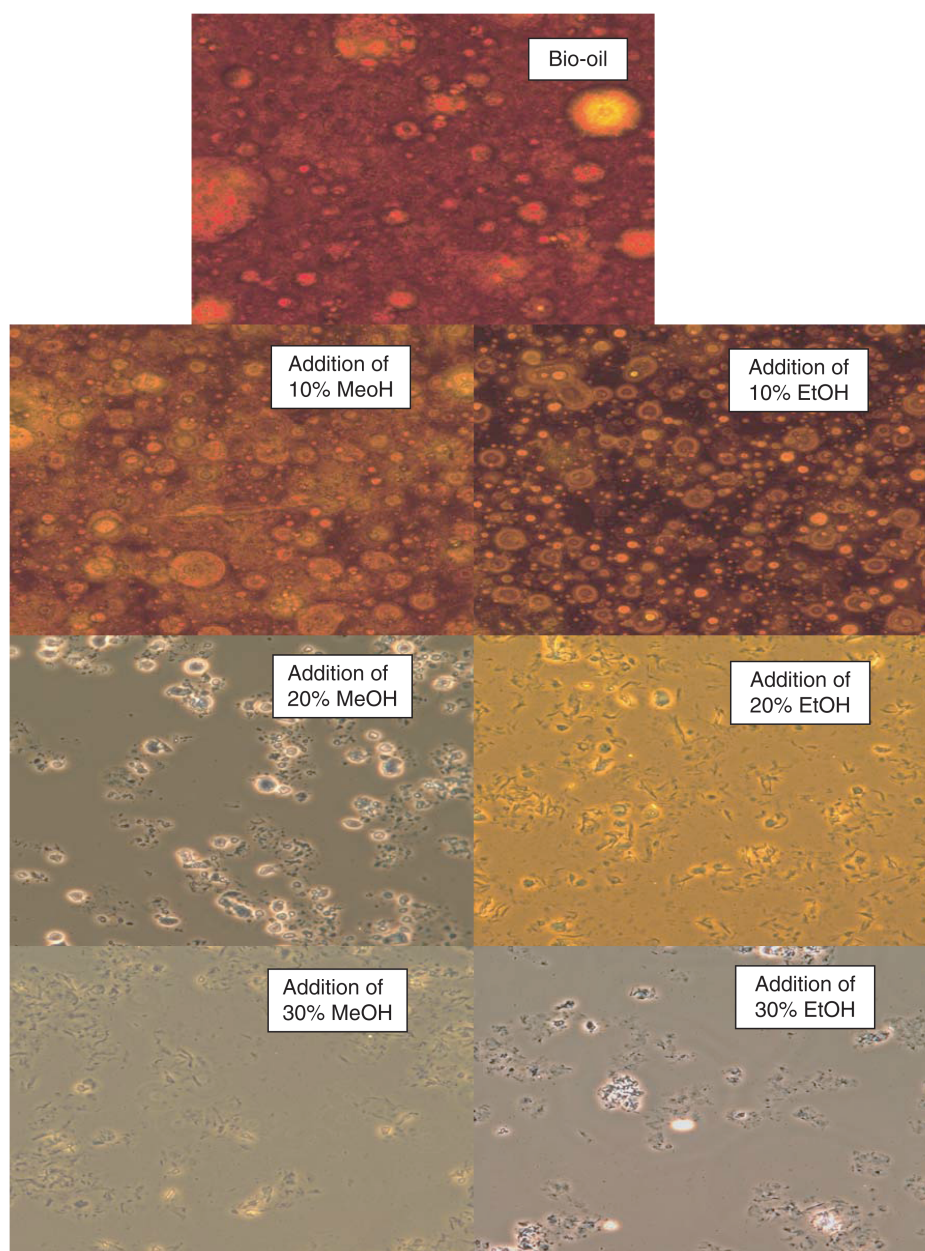
Fig. 1. Microscopic images of bio-oils and bio-oils with solvent addition (×300 magnification).

could not be read easily. Therefore, the dynamic viscosity was measured. Viscosity of our bio-oils was 185 mPa·s at 40°C (or 148 mm^2/s at 40°C, calculated by the dynamic viscosity of bio-oils divided by the density), which is too high for gas turbine. As mentioned earlier, blending with organic solvent such as methanol and ethanol can reduce viscosity.
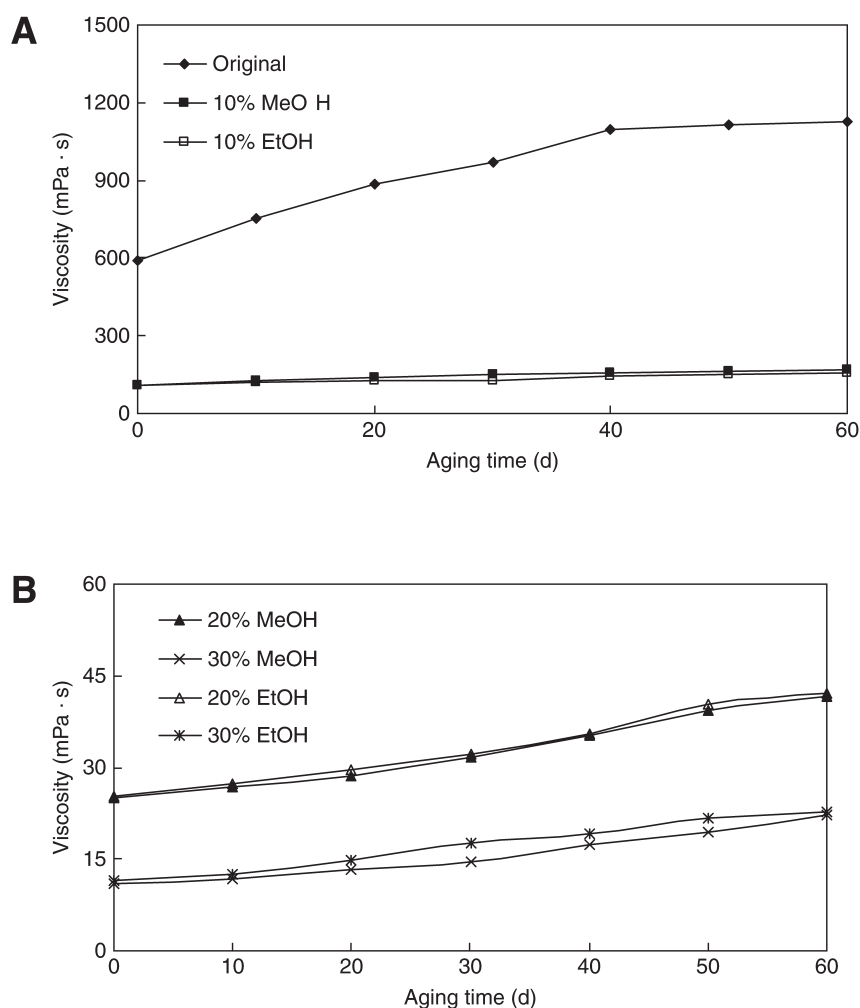
Fig. 2. Viscosity of bio-oils and bio-oils with solvent addition vs ageing period at room temperature.

It was found that the viscosity of the 10% methanol–bio-oil mixture was 3.7 mm^2/s at 40°C, which should satisfy the atomization requirements.

Homogeneity

Bio-oils from microwave pyrolysis appear to be a homogeneous liquid with black solid particles suspended in the liquid as revealed by the microscopy study (Fig. 1). These particles are char residues, or ashes and minerals entrained in the pyrolytic vapors emitted from the pyrolytic reactions. Some solid particles may form through crystallization and precipitation during storage. The solids content can be controlled with filtration before or after oil recovery process. Microscopic analysis of the 10–30% methanol or ethanol–bio-oil blends shows that methanol or ethanol improved the quality of the dispersion and the homogeneity. Moreover, the methanol
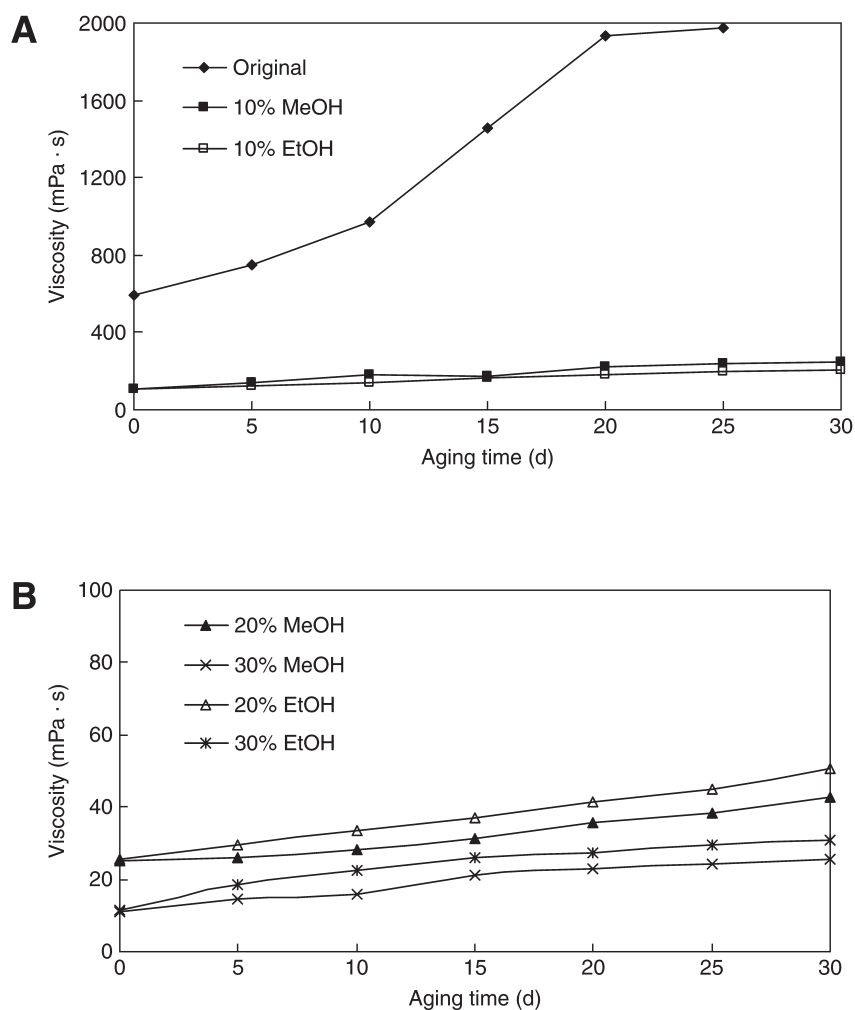
Fig. 3. Viscosity of bio-oils and bio-oils with solvent addition at 40°C.

or ethanol reduces the size of the aqueous phase droplets *(9)*. The water droplets in the bio-oil sample will agglomerate gradually and form larger size droplets, ultimately leading to sedimentation during storage. Methanol or ethanol is miscible with both components of the oil system and aqueous phase system, helping to form small particle size droplets, and hence, decrease considerably the sedimentation velocity and increase the stability of the emulsion. The comparison between the pure bio-oils and the blends indicates an increase in the number of droplets, which is translated to an increased homogeneity of the sample.

Aging

Organic compounds in bio-oils samples can continue to react to form larger molecules during storage over time, which can contribute to
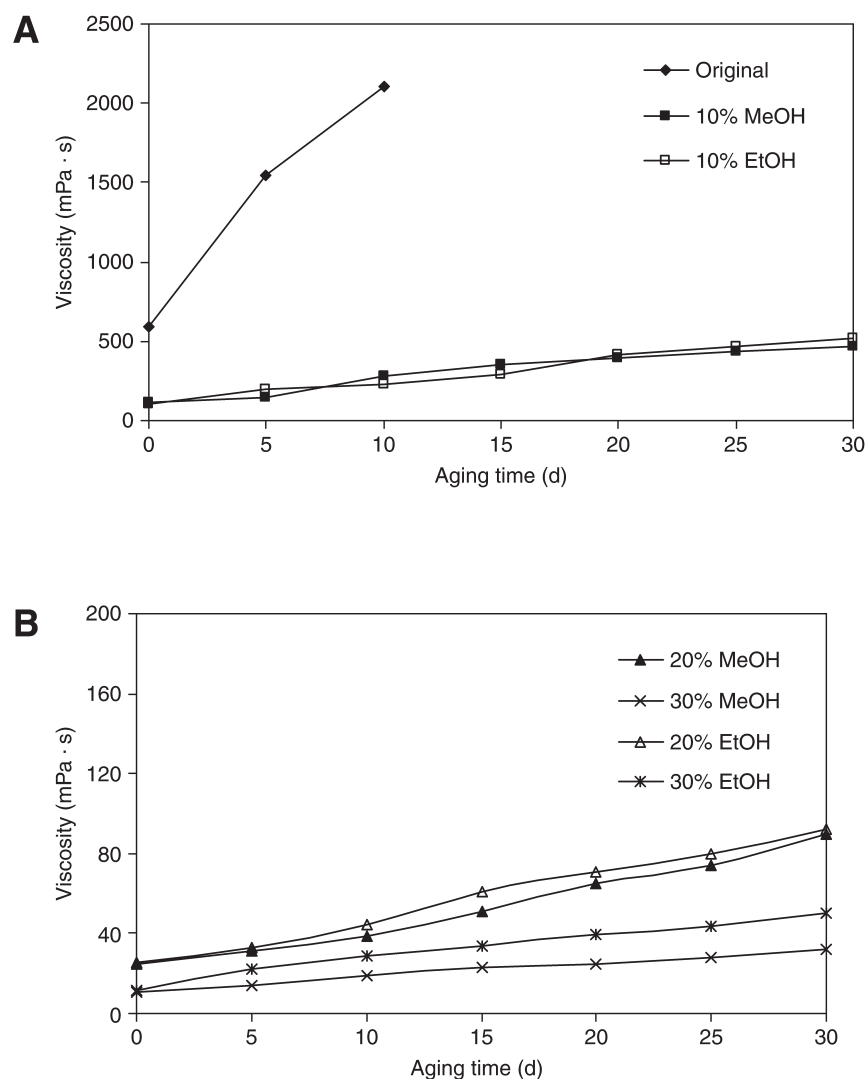
Fig. 4. Viscosity of bio-oils and bio-oils with solvent addition at 60°C.

increase in viscosity and water. The main chemical reactions are etherification and esterification occurring between hydroxyl, carbonyl, and carboxyl group components, in which water is a byproduct *(7)*. Polymerization of double-bonded components also happened because of the instability of those chemicals.

The dynamic viscosity of the pure bio-oils and the solvent/oil blends was measured as a function of the aging time at different temperatures (Figs. 2–4). The results indicated that the viscosity of the pure bio-oils increased dramatically during the first 40, 20, and 10 d at storage temperatures of 22, 40, and 60°C, respectively, followed by a slow increase or a plateau. Addition of methanol or ethanol decreased the viscosity substantially.
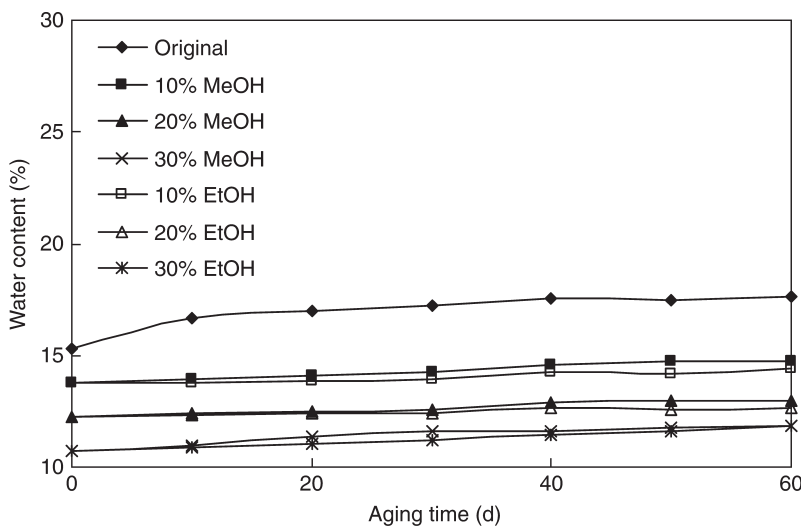
Fig. 5. Water content of bio-oils and bio-oils with solvent addition vs ageing period at room temperature.

The viscosity of bio-oils was reduced by the addition of solvent (regardless of methanol or ethanol), not only because solvent has a low viscosity, but also because they are good solvents for bio-oils. For example, a concentration of 10% methanol in bio-oils produced a mixture with a viscosity five times lower than that of original bio-oils, whereas 20% methanol in bio-oils decreased the viscosity of bio-oils by a factor of 24. The addition of methanol or ethanol also slowed down the increase in viscosity during storage.

Figures 5–7 show the water content of the pure bio-oils and the blends during the storage at different temperatures. The water content of bio-oils was reduced by the addition of solvent *(12)*. The observed water content increase from 15.27 to 17.60% during the 2 mo storage, was considered small. The increase was higher at higher storage temperatures. Similar results were obtained by Czernik et al. *(13)*. The aging rate (increasing rate for viscosity and water content) depends on bio-oils composition, which in turn affects the feedstock, pyrolysis types and conditions, the efficiency of solid removal and product collection, and storage conditions especially the storage temperature, which can affect exponentially the rates of chemical reactions during storage.

Phase Stability

Phase separation may occur during a long-term storage of bio-oils, especially at high temperatures *(8)*. Our observation indicates that a low-viscosity water-rich layer appeared on the top whereas a high-viscosity tar-rich layer appeared at the bottom of the pure bio-oils. Such phase separation phenomenon occurred after 30 d at 40°C and 15 d at 60°C. The high-molecular weight tar may further become a gum and ultimately a
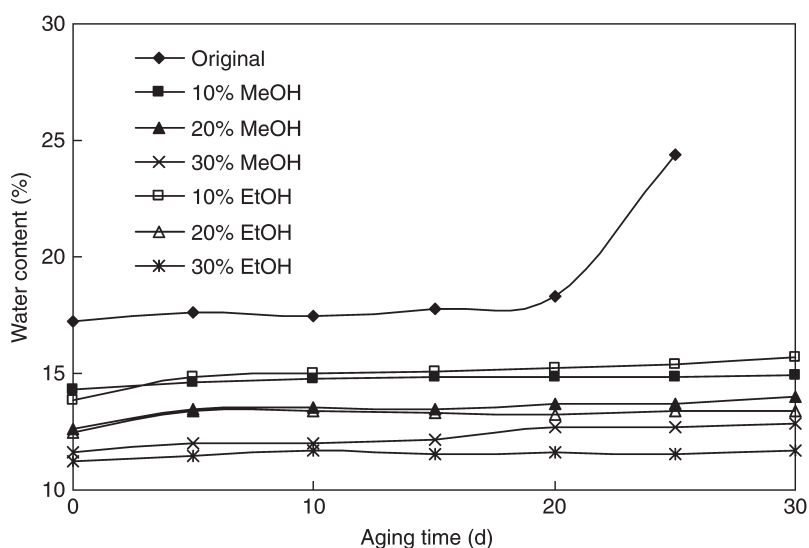
Fig. 6. Water content of bio-oils and bio-oils with solvent addition at 40°C.
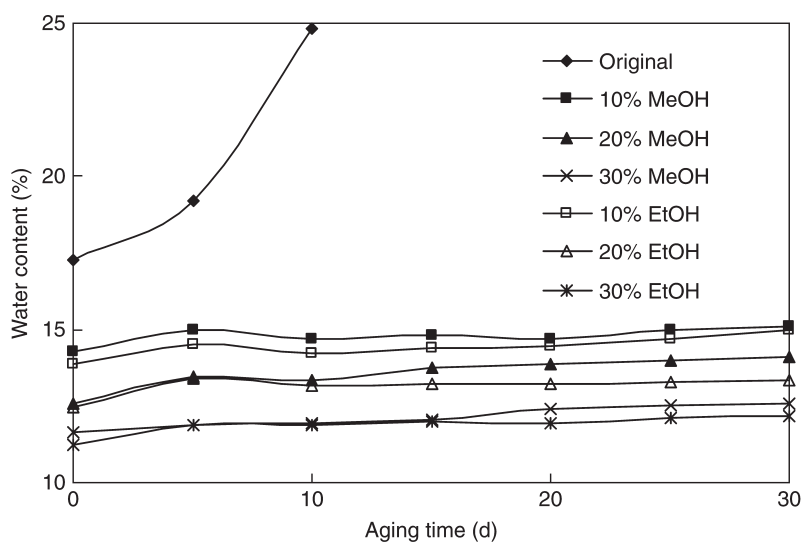

Fig. 7. Water content of bio-oils and bio-oils with solvent addition at 60°C.

carbonaceous clot. For the solvent–bio-oil blends, no phase separation was observed after 30 d of storage at 40°C and 60°C, suggesting that addition of methanol and ethanol to the pure bio-oils inhibited phase separation. The results suggested that a 10% methanol or ethanol addition to the bio-oils would be sufficient to prevent phase separation. This is particularly important to bio-oil storage at high temperatures.

Conclusions

In this study, the physical and chemical properties of the bio-oils produced from a microwave-assisted pyrolysis of corn stover were investigated. The ash content and solids content in the bio-oils were relatively low. The gross heating value was about 41% of the petroleum oil. The bio-oils had undesirable pH, water content, and viscosity values if the bio-oils are to be used as gas turbine fuel. The bio-oils experienced an increase in viscosity accompanied by phase separation over a 30–60 d storage. Blending methanol or ethanol into the bio-oils was proved to improve the properties and stability of the bio-oils. Our study showed that addition of 0methanol or ethanol enhanced the homogeneity and greatly reduced the viscosity of the bio-oils, and slowed down the aging process. The solids content and large particles can be reduced through filtration before and/or after bio-oil recovery process. We believe that with further research and development, bio-oils from microwave-assisted pyrolysis of biomass are a promising candidate for gas turbine fuel and home heating oil.

Acknowledgment

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