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Rheological Characterization of Bio-Oils from Pilot Scale Microwave Assisted Pyrolysis

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1. Introduction

Renewable energy is gaining importance in satisfying environmental concerns and addressing economical concerns over fossil fuel usage. Lignocellulosic materials are the most abundant renewable resources on earth (Lynd et al., 2005). Energy can be obtained from biomass either biochemically or thermochemically. In the biochemical process, pretreatment of biomass is a necessary and the first step in opening up structure of the biomass cell wall to permit the access of enzymes to cellulose and hemicellulose. Pyrolysis, gasification, and combustion are the three main thermochemical processes to get energy from biomass. Combustion has a maximum efficiency of more than 30% (Yu et al., 2007). Because gasification offers higher efficiency compared to combustion, it has attracted a high level of interest (Bridgwater, 2004). According to Wornat et al (1994), the burning of bio-oils produced through the pyrolysis of biomass is more efficient. Bio-oil also offers advantages in storage and transport and in its versatility as an energy carrier and as a source of chemicals (Bridgwater, 2004).

The thermochemical process can convert a low-carbohydrate or non-fermentable biomass to alcohol fuels, thus adding technological robustness to efforts to achieve the 30 x 30 goal. Pyrolysis is an endothermic reaction wherein thermal decomposition occurs in the absence of oxygen. It is always the first step in gasification and combustion, wherein partial or total oxidation of the substrate occurs. Gas is the main product (85%) in gasification, whereas bio-oil (70-80%) is the main product in most types of pyrolysis. The yield of pyrolysis products such as syngas/ producer gas (mixture of CO and H₂), bio-oil, and bio-char (charcoal) would vary depending upon the pyrolysis methods (conventional, fast, vacuum, flash, and ultra), biomass characteristics (feedstock type, moisture content, particle size), and reaction parameters (rate of heating, temperature, and residence time). Bridgwater (2003) listed four essential features to get bio-oil from fast pyrolysis: very high heating rates (1000°C/s), high heat transfer rates (600-1000 W/cm²), short vapor residence times (typically <2 s), and rapid cooling of pyrolysis vapors and aerosols. Because the heart of a fast pyrolysis process is the reactor, during the last two decades several different reactor designs to meet the rapid heat-transfer requirements have been explored. Achieving very high heating and heat transfer rates during pyrolysis usually require a finely ground biomass feed.

Pyrolysis using microwave irradiation is one of the many ways of converting biomass into high value products and chemicals. Not only does microwave assisted pyrolysis (MAP) not require a high degree of grinding (e.g., large chunk of wood logs can be used) as required in

other fast pyrolysis, it also can handle mixed feedstocks (e.g., municipal solid wastes). Fast internal heating by microwave irradiation has an advantage over conventional heating. Moreover, microwave energy deposition in the dielectric loss mode of heating can cause spatially uniform heating (Miura et al., 2000) and is easy to control. The other technical advantages of MAP over conventional pyrolysis include the lack of necessity of size reduction (powder form) and the absence of need for agitation and fluidization; thus the resulting pyrolytic gas and bio-oils that are cleaner than those from gasification and conventional pyrolysis. The absence of a carrier gas for fluidization results in a higher heating value of the syngas produced. Because microwave heating is a mature technology, developing a microwave heating system for biomass pyrolysis would have a low cost.

Both Bioenergy (International Energy Agency) studies and work performed in Finland have estimated bio-oil to be the lowest-cost liquid biomass-based fuel. The targeted final application would dictate the desirable quality of bio-oils. For example, the calorific value, viscosity, density, surface tension, and distillation characteristics are of critical importance for fuel applications (Garcia-Perez et al., 2006a). The above characteristics can be achieved if bio-oil has (i) a low solid content, (ii) good homogeneity and stability, and (iii) a reasonably high flash point. Solantausta et al (1994) concluded that the use of bio-oil in gas turbines can be increased by optimizing their physical and chemical properties (ash content, alkali content, heating value, and viscosity). The viscosity of bio-oil affects the spray pattern and droplet size. A high viscosity of bio-oil results in high line pressure drops, thereby requiring the fuel pump to work harder in order to maintain a constant flow rate. Doll et al (2008) derived an equation describing automation characteristics of the fuel consisting of terms like characteristic number (K), density (ρ), Weber number (We), Reynolds number (Re), surface tension (γ), and kinematic viscosity (ν). In order to get the desired low characteristic number (K), two physical parameters of the fuel that must be governed are the kinematic viscosity (ν) and surface tension (γ). Moreover, viscosity is considered as the more important of these two factors. The viscosity of bio-oils can vary over a wide range (35-1000 cP at 40 °C) depending on the feedstock and process conditions (Bridgwater, 2004; Czernik & Bridgwater, 2004). According to Diebold (2002), an efficient collection of volatile components during bio-oil production results in a bio-oil with more low-molecular weight components with lower viscosity, better solvency properties, and possibly better storage properties.

In general, the production of bio-oil through pyrolysis is a thermodynamically non-equilibrium process. This process requires only a short residence time in a high temperature zone followed by rapid thermal quenching to produce a bio-oil that is also not at equilibrium (Ringer et al., 2006). The presences of many reactive organic compounds in the bio-oil interact to achieve equilibrium during storage. The reactions result in the formation of larger molecules and consequently increase the viscosity of the bio-oil (Diebold & Czernik, 1997; Ringer et al., 2006). Because of the high oxygen (40-50 wt %) and water content (15-30 wt %) and the low H/C ratios, bio-oils cannot be used as transportation fuels directly without prior upgrading. As mentioned earlier additional obstacles are the limited stability of the bio-oils under storage conditions due to the presence of unsaturated compounds and their minor miscibility with conventional liquid fuels (Samolada et al., 2000). Catalytic biomass pyrolysis is a promising approach due to the elimination of costly condensation and re-evaporation procedures prior to bio-oil upgrading (Samolada et al., 2000; Lu et al., 2009a).

Several studies have indicated that the viscosity of bio-oil depends on the type of feedstocks, type of pyrolyzer, and pyrolysis conditions. The type of feedstock is the main variable that

affects the quality of the bio-oil apart from the postproduction processing techniques. In order to gain a better understanding of the effect of feedstock on product quality, a comparison of feedstocks is needed (Oasmaa et al., 2005a). Accordingly, the current study was undertaken to compare the viscosity of bio-oils produced from different feedstocks through microwave pyrolysis and to characterize them using storage and loss moduli.

1.1 Significance of bio-oil viscosity

Viscosity of a bio-oil is the measure of its internal friction which resists the flow of it. Viscosity is an important fuel property that should be considered when attempting to design and select handling, processing and transportation equipment. Viscosity of bio-oil affects the operation of fuel injection equipment, particularly when the increase in the viscosity affects the fluidity of fuel at low temperatures. Again, the quality and practical application of bio-oil as fuel is closely dependent on its viscosity and the elemental compositions i.e., the lower viscosity and oxygen content is desirable (Ertas & Alma, 2010). In general, bio-oil has high viscosity as compared to crude oil and diesel fuel (Onay & Kockar, 2006; Parihar et al., 2007; Pootakham & Kumar, 2010a,b). Pootakham and Kumar (2010a) reported that the loading equipment of the petroleum product such as gasoline and diesel fuels operates between 0.9 and 1.3 m³/min, whereas they can be operated for bio-oil at a volume flow rate of 0.6 m³/min and an operating pressure of 205 kPa (or 30 psi) for safety (Jones & Pujadó, 2006). Bio-oil is more viscous than crude oil at room temperature; however its viscosity is very similar to that of crude oil in a temperature range of 35–45°C, (Bridgewater, 1999; Thamburaj, 2000; Pootakham & Kumar, 2010a,b). In order to transport the bio-oil in pipeline, the temperature of the pipeline should be maintained in the range of 35–45°C to keep the viscosity similar to that of crude oil (Pootakham & Kumar, 2010a, b). According to Thangalazhy-Gopakumar et al (2010), viscosity of bio-oil is relatively higher than that of diesel (0.011 Pa.s) and gasoline (0.006 Pa.s). In general, high viscosity fuel results in poor atomization and incomplete combustion, formation of excessive carbon deposits on the injection nozzles and the combustion chamber, and contamination of the lubricating oil with unburnt residues. The viscosity of the fuel directly influences atomization and mixing in the combustion chamber. In fuel application, the lower the viscosity, the easier it is to pump and to atomize and achieve finer droplets (Ji-Lu, 2008). Hence bio-oils in their original form are not suitable for use in modern diesel engines (Özaktas et al., 1997). Because of their high acidity, low thermal stability, low calorific value, high viscosity, and poor lubrication characteristics limit their use as transportation fuel (Garcia-Perez et al., 2006b). Oasmaa et al (2005) stated that for engine application, the viscosity should be in the range of 10-20 cSt with a solids content of less than 0.1 wt%. As is known, bio-oils are entirely different from petroleum fuels. There is a necessity to establish fuel specifications for commercial application of bio-oils as liquid fuels. The specifications should include the most critical properties such as viscosity, lubricity, homogeneity, stability, heating value, pH, water, flash point, solids, and ash (Qiang et al., 2008).

The viscosity of bio-oil varies depending on the temperature, feedstock, water content of the oil, amount of light ends that have been collected and the extent to which the pyrolysis oil has aged (Ji-Lu, 2008). For example, bio-oil produced from *P. indicus* and *F. mandshurica* had a kinetic viscosity of 70–350 mPa s and 10–70 mPa s separately, and bio-oil produced from rice straw had a minimum kinetic viscosity about 5–10 mPa s, which is mainly due to high water content in bio-oil from rice straw (Luo et al., 2004). The presence of water has both

negative and positive effects on the storage and utilization of bio-oils. The negative effects are, it lowers heating values, causes phase separation, increases ignition delay, and reduces combustion rates and adiabatic flame temperatures during the combustion process. Further, it leads to premature evaporation and subsequent injection difficulties during the preheating process. The positive effects are, it reduces viscosity, facilitates atomization, and reduces pollutant emissions during combustion (Calabria et al., 2007). Moreover, OH radicals from water can inhibit the formation of soot and can also accelerate its oxidation.

According to Sensöz and Kaynar (2006), viscosity of the bio-oils is related to fatty acid chain length and number of saturated bonds. In general, the density of bio-oil is higher than that of water confirms that it contains heavy fractions (Sensöz et al., 2006). The lignin content of original feedstock has a positive influence on molecular weight and viscosity of bio-oil (Fahmi et al., 2008). Recently, Ertas and Alma (2010) compared the average molecular weight and molecular weight distribution of laurel extraction residues bio-oil (664 g mol/l and 1.52) and found they were very close to those of switchgrass bio-oil of 658 g mol/l and 1.49, respectively (He et al., 2009a). Viscosity of bio-oil increases during storage, due to slow polymerization and condensation reactions, the increase in viscosity is enhanced by higher temperature. The presence of inhibitors (hydroquinone) can dramatically reduce the rate of increase in bio-oil viscosity, due to the suppression of thermal polymerization reactions by the inhibitors (Ji-Lu, 2008). Garcia-Perez et al (2010) observed that the increase in viscosity of bio-oils is due to the solubilization of lignin derived oligomers. The condensation reactions occur ageing increases the water content in bio-oil with time (Garcia-Perez et al., 2002). The instability may be attributed to the presence of alkali metals in the ash, which are being carried over/entrained by the char particles with the vapors. These alkali metals catalyze the polymerization reactions and thereby increase the viscosity (Diebold, 2002).

Simple methods such as addition of polar solvents, diesel or other fuels can address some of the undesired bio-oil characteristics. Polar solvents, such as methanol or ethanol, can improve the volatility and heating value and decrease the viscosity and acidity. The addition of ethanol improves the volatility, stability and heating value and decreases the viscosity, acidity and corrosivity (Ji-Lu & Yong-Ping, 2010). The blending of diesel or other fuels can rearrange the viscosity of bio-oil (Onay & Kockar, 2006). In order to improve fuel properties of bio-oils, many methods are under investigation such as emulsification, hydrotreating, and catalytic cracking, which is beyond the scope of this chapter.

2. Materials and methods

2.1 Biomass selection

The low density, strength, and stiffness of aspen make it unsuitable for many structural applications (Mackes & Lynch, 2001). However, aspen has an alternative use as bedding material or feedstock for biofuel or bio-oil. The amount of biomass produced per unit area by canola depends on irrigation and varies from 5 to 10 tons/ha (Enayati et al., 2009). According to the US Canola Association, canola was cultivated on 3.2 million ha during 2009, resulting in 16-32 million tons of canola straw. Early in the US history corn cobs were an important feedstock for heating houses, farm buildings, and small businesses. Now, corn cobs are reemerging as a potential feedstock for direct combustion, gasification, and cellulosic ethanol due to numerous advantages (dense and relatively uniform size, high heat value, and low N and S contents) over many competing feedstocks. The average cob yield is about 14 % of the grain yield and represents about 16 % of the corn stover biomass in a field

on a dry matter basis (Roth & Gustafson, 2010). According to Blaschek and Ezeji (2010), 15% of corn stover is corn cob. Various sources have independently estimated that anywhere from 200 to 250 million dry tons of corn stover are produced per year (Sokhansanj et al., 2002; Kadam & McMillan, 2003). Based on the 15-16% of stover as cobs, the US annual production of corn cob is estimated at 30-40 million metric tons.

2.2 Bio-oil production

All the bio-oils were produced either in batch or continuous microwave assisted pyrolysis (MAP) processes at the University of Minnesota (Figure 1). About 250 g samples were put in a 1000 mL quartz flask, which in turn was placed inside the microwave cavity (Panasonic NN-SD797S). The power level was set at 8 (the output power is about 1000 W). After the sample was microwaved for around 12 minutes, the volatile pyrolyzates were condensed with cool water at temperature of around 4-5 °C. The fraction collected from bottles connected to the bottom of the condensers was termed as the bio-oil. The condensates adhering to the interior wall of the tubes were then washed with ethanol and concentrated at 80°C using a vacuum rotovap (Buchi R-141, Flawil, Switzerland) to a near constant weight, and the concentrate was added to the bio-oil.



Fig. 1. Batch and continuous microwave assisted pyrolysis (Courtesy: Dr. R. Ruan, University of Minnesota, MN, USA)

As mentioned earlier aspen, canola, and corn cob were the feedstocks selected for the bio-oil production. Aspen pellets were used for the production of bio-oil in a batch MAP process. Canola compost pellets were also used in a batch MAP process. All corn cobs were ground to less than 1 cm in size before MAP. Corn cob 1 and corn cob 2 bio-oils were produced using a continuous MAP, where heavy fractions of the bio-oil were not collected. Corn cob 3 bio-oil was produced using a batch MAP, where heavy fractions of the bio-oil were collected. Corn cob 4 was the bio-oil produced in a batch MAP of corn cob pretreated with 4% sulfuric acid; the bio-oil contained more water and furfural than other bio-oil samples. Fig. 2 shows bio-oils from different feedstocks produced through MAP. Heavy fractions of

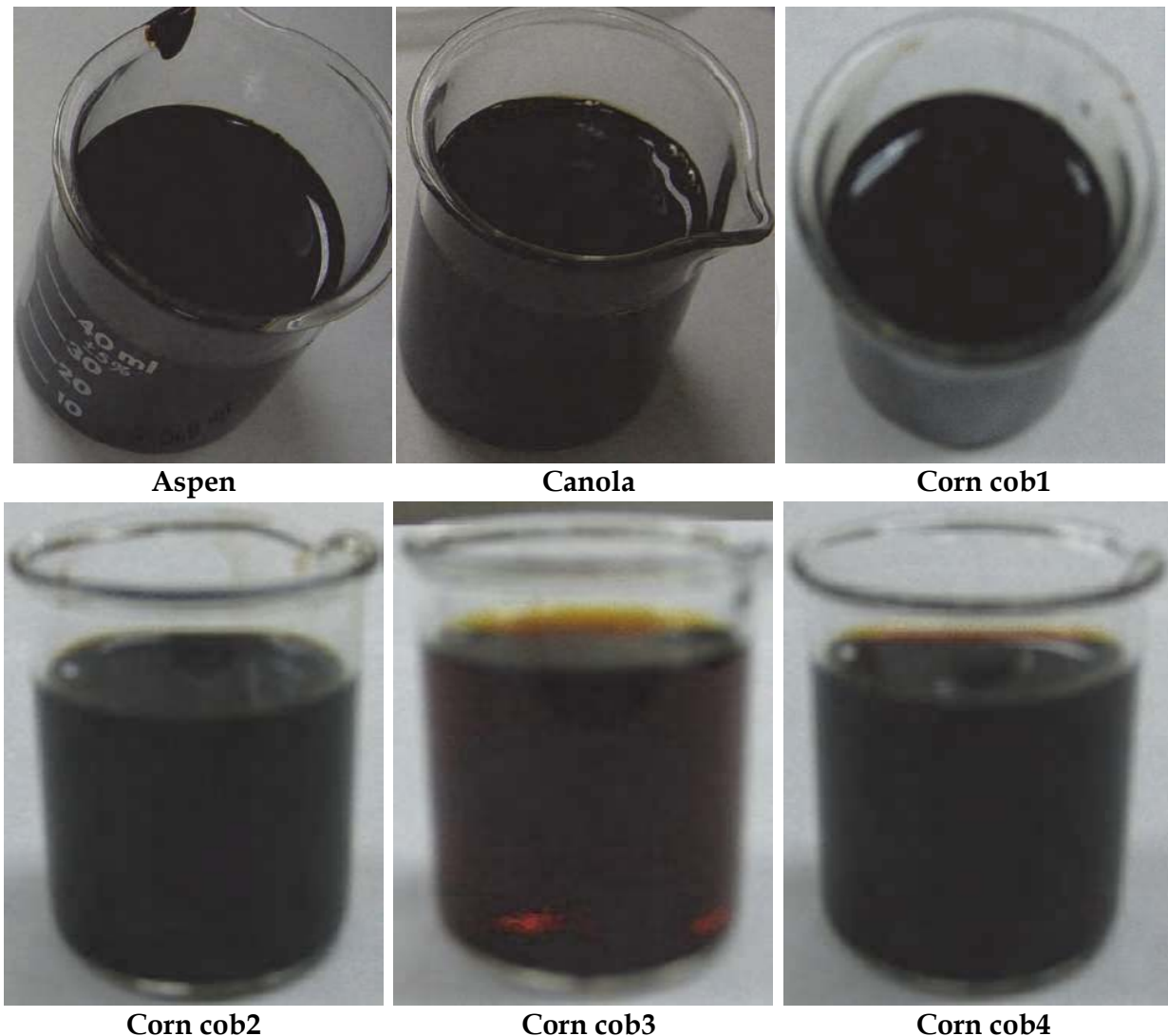


Fig. 2. Samples of bio-oil produced through MAP from different feedstocks

the bio-oils were collected for all batch processes. The bio-oil separated into two phases: about top one-third of the bio-oil was in oily phase and the bottom two-thirds were in aqueous phase. The oily phase is a relatively stable, light emulsion containing water soluble chemicals and light oily components; whereas the aqueous phase is a large molecule oily mixture characterized by high viscosity and water insolubles (Yang et al., 2010). The aqueous phase yield varied between batch (aspen and canola >60%) and continuous (corn cobs 10-20%) production. The aqueous phase yield of corn cobs were in agreement with corn stover (Yang et al., 2010).

2.3 Bio-oil characterization

The viscosity measurement and dynamic rheology were performed on Rheometer (ATS Rheosystems, Rheologica Instruments Inc, NJ) using cup and bob assembly. Approximately 15 mL of sample was filled in cup and shear rate was applied through the bob. The viscosity of bio-oils was tested in rheometer at 20°C with shear rate up to 1 to 200/s. The stress and viscosity was calculated for the shear rate applied using the software. In order to identify the linear viscoelastic region, stress sweep was performed at a constant frequency. For frequency

sweep (1 to 100 Hz), stress was selected from the linear region identified in the stress sweep test. Temperature sweep (20-100°C) was then performed by employing constant stress and frequency identified in the previous steps. The viscoelastic moduli (G' – storage modulus and G'' – loss modulus) were measured as a function of frequency for all the samples. A graph was plotted on logarithmic scales to identify the linear viscoelastic region.

3. Results and discussion

3.1 Effect of temperature on viscosity of bio-oils from different feedstocks

The viscosities of bio-oils produced from different feedstocks were measured at 20, 40, 50, 60, 80, and 100°C and are shown in Fig. 3. In general, the viscosity of bio-oil at 20°C was higher than that of 100°C, irrespective of the feedstocks and with or without catalyst. This observation was in agreement with viscosity of bio-oil from pine wood chips (Thangalazhy-Gopakumar et al., 2010). Bio-oils used in this study had a higher viscosity at lower shear rate and the viscosity decreased exponentially at higher shear rate ($>10/s$) and similar result was reported for bio-oil from pine wood chips (Thangalazhy-Gopakumar et al., 2010). All the bio-oils used in this study showed non-Newtonian behavior as evident from Fig. 1. As mentioned in the introduction section, viscosity plays an important role in atomization through influencing inertial and aerodynamic instabilities. The Sauter mean diameter (SMD) of spray increases with viscosity for Newtonian fluid, whereas elasticity or shear thinning behavior of non-Newtonian fluid would affect the SMD. Thus, it is important to examine the non-Newtonian or viscoelastic nature of bio-oil since it may exhibit these effects during the application. According to Lu et al (2009b), most of the bio-oils behave as Newtonian fluids at temperatures lower than 80°C, whereas all the bio-oils used in this study even at high temperature (100°C) behaved as non-Newtonian fluid. A prevalent shear thinning behavior was observed at 50 and 80°C by Tzanetakis et al (2008) and similar behaviors were observed for all the bio-oils irrespective of the type of process (batch or continuous), with or without catalyst and kinds of feedstocks.

The viscosity of bio-oil between 20, 40, and 80°C were statistically different for all the feedstocks. Although the viscosities of bio-oil from corn cob were different at 20°C, the differences vanished at 80°C. In general, the viscosity of bio-oils produced from different feedstocks decreased with an increase in temperature. Similar trends were reported for bio-oils produced from different feedstocks such as softwood bark (Boucher et al., 2000a, b), sugarcane bagasse (Garcia-Perez et al., 2002), rice husk (Zhang et al., 2006), switchgrass (Boateng et al., 2007), corn stover (Yu et al., 2007), hardwood (Tzanetakis et al., 2008), pine and oak wood and bark (Ingram et al., 2008), pine wood chips (Thangalazhy-Gopakumar et al., 2010), and rice husk (Ji-Lu & Yong-Pong, 2010). When temperature was increased from 20 to 40°C, viscosity of bio-oil from canola showed a minimum decrease of 9% and bio-oil from corn cob 1 showed a maximum decrease of 25%. A further increase in temperature to 80°C resulted in viscosity decrease of 26 and 52%, respectively, for the bio-oil produced from canola and corn cob 1. Bio-oil derived from hardwood showed a similar behavior; however, the decrease was seven fold (Tzanetakis et al., 2008). The bio-oil viscosity measured at 40°C in this study was ten-fold lower than the viscosity (0.02 Pa.s) of the bio-oil produced from (heterotrophic) microalgae (Miao & Wu, 2004). The viscosity of bio-oils produced from different feedstocks though MAP was lower than the light fuel viscosity of 4 cSt (Mohan et al., 2006), the heavy fuel oil viscosity of 50 cSt (Czernik and Bridgwater, 2004), the US #4 fuel oil viscosity of 5.5-24 cSt (Oasmaa et al., 2009), commercial automotive #2 diesel viscosity of 2-4.5 cSt (Islam et al., 2010), diesel viscosity of 0.011 Pa s (Thangalazhy-Gopakumar et al.,

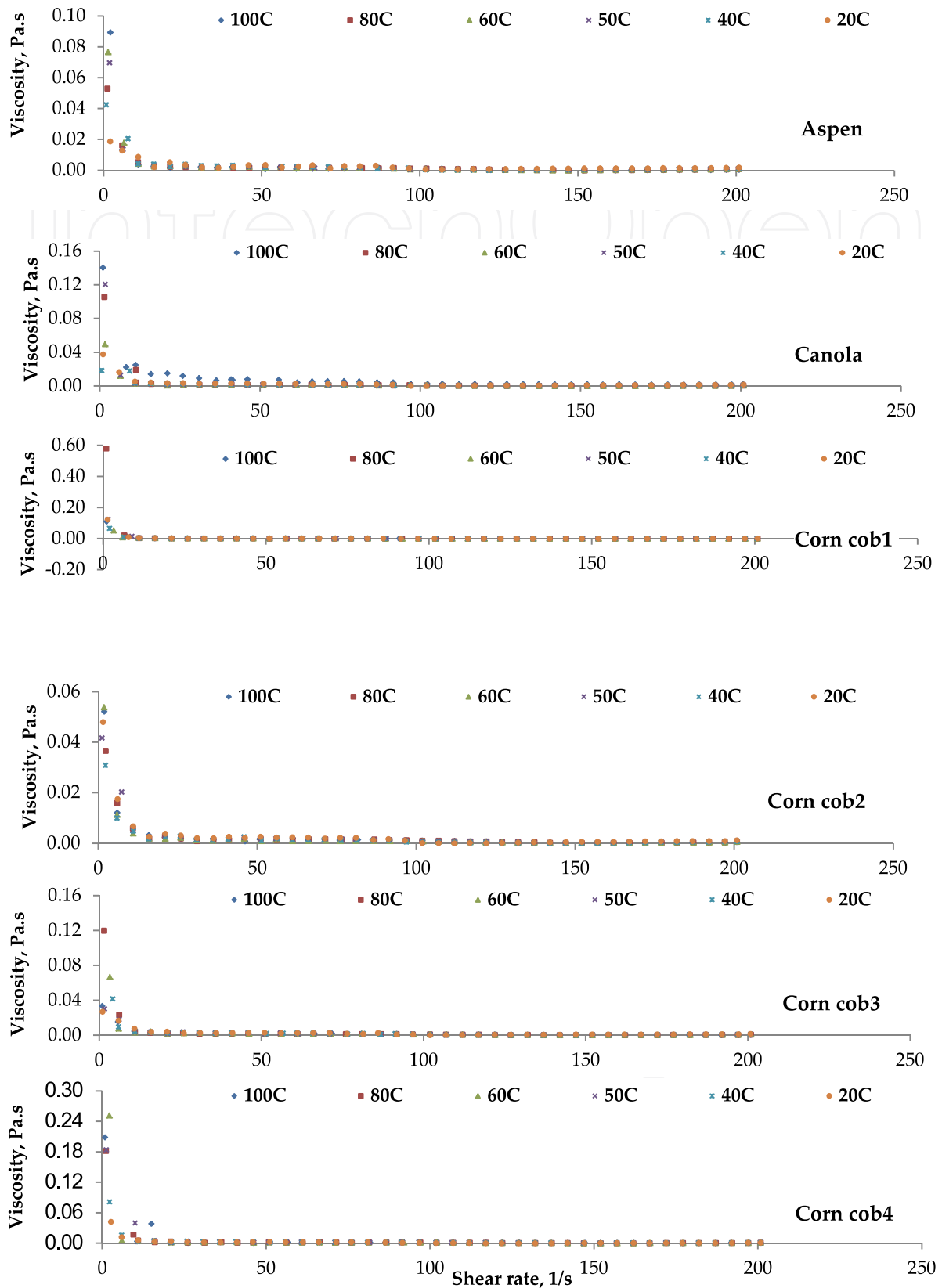


Fig. 3. Viscosity of bio-oils produced from different feedstocks at indicated temperatures

2010), and was higher than JP4 viscosity of 0.88 cSt (Chiaramonti et al., 2007) and gasoline viscosity of 0.006 Pa s (Thangalazhy-Gopakumar et al., 2010) at a temperature of 40°C. Considering the viscosity criteria (15 cSt at 35-45°C and 21.5 cSt at 30°C) presented by researchers (Pootakham & Kumar 2010a; Islam et al., 2010) for loading/handling and pipe transportation, the bio-oils from different feedstocks produced through MAP can be easy to load using existing petroleum loading equipments and easy to transport through pipe also. According to ASTM burner fuel standard, the bio-oil can have a maximum viscosity of 125 cSt at 40°C without filtering (Oasmaa et al., 2009). Considering this limit, the viscosity of the bio-oils used in this study had a much low viscosity and these bio-oils can be used as burner fuel.

Czernik and Bridgwater (2004) reported that the viscosity of bio-oil produced from wood would vary between 40 and 100 cP at 50°C, whereas the viscosity of the heavy fuel oil is 180 cP. As evident from Fig. 3, the viscosity of bio-oils produced from different feedstocks through batch or continuous MAP with or without catalyst had a significantly lower viscosity (1.5-2.2 cP) than the viscosity values reported by Czernik and Bridgwater (2004) and the viscosity of bio-oil (33 cP) from hardwood at 50°C (Tzanetakis et al., 2008). The viscosity of bio-oils used in this study was lower than that of bio-oil from sugarcane bagasse (12.1-28 cSt) measured at 60 and 80°C (Das et al., 2004). This result indicates that the bio-oils produced through MAP can be easily atomized. One possible reason for low viscosity of the bio-oils in this study was the absence of agitation and fluidization in MAP resulted in a clearer bio-oil (free from fine char/particles) than that of conventional pyrolysis.

3.2 Comparison of viscosity from different feedstocks

As noted in Fig. 3, bio-oil from canola had lower viscosity than that of aspen. Among the bio-oils produced from corn cob, the viscosity of bio-oil with catalyst (corn cob 4) was lower than other bio-oils due to more water content. The viscosity of bio-oil produced from corn cob without catalyst was similar to that of liquid phase of canola and it was lower than that of liquid phase of aspen.

All the bio-oils from different feedstocks were behaved as a non-Newtonian fluid. Similar behaviors have been reported for bio-oils (upper layer) obtained from forest residues (Garcia-Perez et al., 2006a) and pine and oak bark (Ingram et al., 2008). However, Ingram et al (2008) reported Newtonian behavior at 25°C for the bio-oils produced from pine and oak wood through auger reactor but at higher temperatures (50 and 80°C) they showed mild shear thinning behaviors. Rheological data of shear rate and shear stress of the bio-oils were fitted according to the Power-Law model

$$\mu = k\gamma^{n-1} \quad (1)$$

where, μ is the viscosity (Pa-s), k is the consistency coefficient (Pa.sⁿ), γ is the shear rate, 1/s and n is the flow behavior index of the fluid (dimensionless). The power law constants for different bio-oils are presented in Table 1. The flow behavior indexes n less than 1 suggests that presence of the pseudoplastic behavior (shear thinning). A possible reason might be breakdown of (waxy) structure would result in low viscosity at high shear rate. In general, the values of flow behavior index are more reliable than that of consistency coefficient (Johnson, 1999). The deviation of flow behavior index from 'unity' indicates the degree of deviation from Newtonian behavior. For shear thinning, the index value can be anywhere between 0 and 1. The smaller the value of n , the greater is the degree of shear thinning (Chhabra & Richardson, 1999). Considering the above points, canola aqueous phase

exhibited strong shear thinning behavior than that of the rest. In general, the bio-oils from corn cob approaches Newtonian behavior as the n values were close to unity.

Bio-oil	Power law constants	Temperature, °C					
		20	40	50	60	80	100
Aspen	k	0.019	0.030	0.040	0.071	0.063	0.153
	n	0.456	0.229	0.126	0.003	0.031	0.298
Canola	k	0.065	0.105	0.094	0.093	0.128	0.223
	n	0.132	0.077	0.085	0.056	0.179	0.058
Corn cob 1	k	0.030	0.047	0.040	0.058	0.123	0.103
	n	0.289	0.107	0.144	0.034	0.165	0.175
Corn cob 2	k	0.061	0.097	0.039	0.046	0.067	0.103
	n	0.084	0.074	0.143	0.056	0.083	0.173
Corn cob 3	k	0.040	0.070	0.048	0.05	0.107	0.070
	n	0.250	0.010	0.095	0.08	0.131	0.093
Corn cob 4	k	0.059	0.066	0.089	0.091	0.046	0.048
	n	0.043	0.044	0.063	0.146	0.008	0.001

Table 1. Power law constants of the bio-oils at different temperatures

3.3 Comparison of viscosity measurements and bio-oil viscosities

Accurate measurement of the viscosity of bio-oil/fuel is essential for the proper operation of fuel supply systems and atomisers. The viscosity of bio-oil can be measured according to the ASTM D 445 using the following equation

$$\eta = \pi Pr^4 t / 8lv = \pi h \rho gr^4 t / 8lv \quad (2)$$

where η is the viscosity (dynes/cm² or poise), v is the volume of liquid (c.c.), t is the liquid flowing time (s), r is the radius of narrow tube (cm), l is the length of narrow tube (cm). This is most widely followed method, as evident from table 2. The viscosity of bio-oil can be measured using capillary or rotational viscometers and they are reported as kinematic (cSt) or dynamic viscosity (mPa.s). The kinematic viscosity of the bio-oil can be converted into dynamic viscosity if the density (kg/dm³) of bio-oil is known at a given temperature using the following formula

$$\eta(\text{mPa.s}) = \eta(\text{cSt}) * \rho(\text{kg/dm}^3) \quad (3)$$

Pyrolysis type and conditions	Feedstock	Viscosity method	Temp, °C	Viscosity, cSt	Density method	Density at temp kg/ m ³	Ref
Fluidized bed fast pyrolysis, 480°C	Switchgrass	ASTM D445	40	22.14			Boateng et al., 2007
		-do-	50	13.11			
		-do-	100	2.54			
Fluidized fast pyrolysis, 420-540°C	Rice husk	ASTM D445-88	20	128		1190	Ji-lu, 2007
Fluidized bed reactor, 300-600°C	Jute stick		30	2.34 cP	Density measurement bottle	1.11 g/ mL at 30°C	Asadullah et al., 2008
Fluidized bed reactor, 350-375°C	Mallee wood	Fluids spectrometer RFS II rheometer	22	40-98 cP			Garcia-Perez et al (2008)
Fluidized bed fast pyrolysis, 450-550°C	Switchgrass	ASTM D445 Schott Ubbelohde capillary viscometer	40	17-28.2	ASTM D1217	1.11-1.17	He et al., 2009a
Fluidized bed fast pyrolysis	Switchgrass	ASTM D445	40	37.6	ASTM D4052	1190 at 15°C	He et al., 2009b
Bubbling fluidized bed pyrolyzer, 450-550°C	Guayule		60	2472.7		1.1382 g/ mL	Boateng et al., 2009
Auger reactor, 450°C	Pine wood	Stony Brook Model PDVa-100	50	55.2	Std	1.18 g/ mL	Hassan et al., 2009a
Bubbling fluidized bed fast pyrolysis , 500°C	Barley straw	Graber Mini Visif automatic microviscometer	40	23.5			Mullen et al., 2010
Fast pyrolysis VTT, 520°C, 1-2s	Barley hull		40	10.2			
Fast pyrolysis VTT, 520°C, 1-2s	Pine		20	100-200		1100-1300	Oasmaa et al., 2004
Fast pyrolysis VTT, 520°C, 1-2s	Forest residue		40	15-50			Oasmaa et al., 2005b
Fast pyrolysis VTT, 520°C, 1-2s	Forest residue	ASTM D445	20	100			Oasmaa & Kuoppala, 2003
Fluidized bed flash pyrolysis, 530°C	Wheat straw	-do- ASTM D445	40	30			
			50	11	ASTM D 4052	1.186 kg/ dm ³ at 15°C	Siplia et al., 1998

Pine wood	-do-		46				1.266 kg/ dm ³	
Hard wood	-do-		50				1.233 kg/ dm ³	
Rice husk	Glass capillary viscometer		13.2				1.14 g/ mL at 30°C	Lu et al., 2008
Sugarcane bagasse	Capillary viscometer		7.1 cP				1167	Anto & Thomas, 2009
Beach wood chips	Dynamic stress rheometer (SR 200), shear rate 5/ s		3.6-6.9 cP				1200-1230 at room temp	Guillain et al., 2009
Oak wood	Brookfield digital viscometer model LVTD		159 cP				1.29 g/ cm ³	Czernik et al., 1994
Rape seed cake	ASTM D88		42.6				900	Çulcuoglu et al., 2005
Oil palm empty fruit bunch	ASTM		13.52				1.031 g/ cm ³	Khor et al., 2009
Softwood bark	ASTM D445-88 Cannon Fenske upflow viscometer (modified) Bohlin rheometer (0.5 Pa)		128				1.066 g/ mL at 20°C	Boucher et al., 2000a
	-do-		38				1.051 g/ mL	
	-do-		24				1.043 g/ mL	
	-do-		15				1.034 g/ mL	
	-do-		7.5					
Vacuum pyrolysis, 500°C, 14 kPa	ASTM D445 Cannon Fenske upflow viscometer		85					Boucher et al., 2000b
	-do-		24					
	-do-		8					
Vacuum pyrolysis, 530°C, 40 kPa	ASTM D445-88 Brookfield viscometer model LVDV III+		62				1.188	Ba et al., 2004
	-do-		15					
Vortex reactor-NREL	Brookfield viscometer # 18 spindle, shear rate 79/ s		22 cP				1.2 g/ cc	Diebold & Czernik, 1997
Bagasse			510.3				1.0904 g/ mL	

Auger reactor, 500°C, 5.9 min	Pine chips	Brookfield synchronometric LVT viscometer	25	125.6 cP	Densitometer	1.183	Garcia-Perez et al., 2007
Auger reactor, 450°C, 30 s	Pine pellets	-do-	25	44.8 cP	Pycnometer ASTM D4052	1.236	Ingram et al., 2008
	Pine wood	Brookfield viscometer LV-DV1+, Rheometer, TA instruments Model 1000N	50	60.9 cP			
Auger reactor, 450°C	Oak wood	-do-	50	41.6 cP	ASTM D4052	1.20 g/cc	Bhattacharya et al., 2009
	Pine bark	-do-	80	70 cP		1.17 g/cc	
	Oak bark	-do-	80	131 cP		1.20 g/cc	
	Pine wood	Stony Brook 200 5B viscometer		80.7		1.19 g/mL	
Auger reactor, 450°C	Pine wood	Stony Brook viscometer model PDVa-100	40	30			Hassan et al., 2009b
Microwave, 600W, 2450Hz, 40 min	Pine bark	-do-		137.9	ASTM 369 Piconometer	1.25 g/mL	Yu et al., 2007
	Cottonwood	-do-		77			
	Cottonwood bark	-do-		472.7			
	Corn stover	ASTM D445 Rotational viscometer Brookfield DV-E	20	1270 cP			
Fast pyrolysis 530 °C, 12 kPa	Sugarcane bagasse	-do-	40	185 cP	ASTM 369 Piconometer	1211	GarciaPerez et al., 2002
		-do-	50	60 cP			
		-do-	80	34 cP			
Slow pyrolysis 500°C, 10°C/ min	Olive waste	ASTM D445-88 Cannon Fenske upflow viscometer	20	116.5	ASTM D1298	1070 at 15°C	SensÖz et al., 2006
		-do-	40	26.7			
		-do-	60	11.2			
		-do-	80	5.4			
		-do-	50	51			
Fixed bed reactor 500°C, 40°C/ min, 30 min	Rapeseed	ASTM D445-88	50	43	ASTM D1298	918 at 30°C	SensÖz et al., 2000
		ASTM D445-88	50	225			
500°C, 50°C/ min, N ₂ flow rate of 100 cm ³ / min	Safflower seed press cake	ASTM D445-88	50	225	ASTM D4052	1079 at 15°C	SensÖz & Angin, 2008

Fixed bed fire tube heating pyrolysis, 475°C	Bagasse	ASTM D445	21.5	ASTM D189	1150	Islam et al., 2010
Fixed bed Pyrolysis 500°C, N ₂ flow rate of 200 mL/ min	Bagasse	ASTM D445	2.25-3.90 cP	Density measurement bottle	1050-1130 at 20°C	Asadullah et al., 2007
Continuous autothermal fast pyrolysis 120 kg/ h, 475°C	Rice husk	Glass capillary viscometer	13.2	Densitometer	1.14 g/ ml at 30°C	Quang et al., 2008
Fixed bed reactor 500°C, 10°C/ min, N ₂ flow rate of 100 mL/ min	Laurel	ASTM D445-88	61	ASTM D4052	1133 at 15°C	Ertas & Alma, 2010
Fixed bed reactor 550°C, N ₂ flow rate of 173 cm ³ / min	Bagasse	ISO 3904 Cannon 5R-33 viscometer	232.3	ASTM 5002	1254.2 at 20°C	Parihar et al., 2007
Flash pyrolysis under N ₂ 600°C	Rapeseed	ASTM D445-88	36	ASTM D1298	984 at 30°C	Onay & Kocakar, 2006
Fixed bed reactor 400°C, 50°C/ min	Soybean oil cake	ASTM D445-88	72.38	ASTM D4052	1107 at 15°C	Sensoz & Kaynar, 2006

Kinematic viscosity- cSt; Dynamic viscosity-cP

Table 2. Comparison of viscosity measurement and bio-oil viscosity produced from various feedstocks through different pyrolysis

According to ASTM D445, the viscosity of standard fuels, which are Newtonian fluids, is typically measured as kinematic viscosity. Leroy et al (1988) conducted extensive studies on rheological characterization of several bio-oils from wood and concluded that those bio-oils exhibited an essentially Newtonian behavior at the shear rate range of 1 to 1000/s. In contrary, bio-oils used in this study showed shear thinning behavior. For Newtonian fluid, the viscosity remains constant with increasing shear rate. Radovanovic et al (2000) reported a procedure to measure bio-oil viscosity using falling ball viscometer. Recently, Osamaa et al (2009) recommended using Cannon-Fenske viscometer tubes because the flow direction in these tubes compared to Ubbelohde tubes ensured more accurate results with dark coloured liquids. No prefiltration of the sample is required if the bio-oil is visually homogenous. Elimination of air bubbles before sampling and an equilibration time of 15 min are essential for viscosity measurement at a given temperature. Comparison of viscosity measurement and viscosity of bio-oils from produced different feedstocks through different pyrolysis reactors are presented in Table 2. Bio-oil density measurement and density values are also included for converting the viscosity from kinematic to dynamic units. According to ASTM D445-88, viscosity should be measured at 20 and 40°C, as seen from the table the viscosity was reported at different temperatures ranging from 20 to 100°C. The viscosity of bio-oils used in this study had lower viscosity than the viscosities listed in the table irrespective of temperatures.

3.4 Stress and frequency sweep

In general, the linear limits of viscoelastic behavior are determined by identifying the range of stress values over which G' and G'' are constant and thus independent of stress. Storage and loss moduli of bio-oil from different feedstocks as a function of shear stress are depicted in Fig. 4. Shear stress from 10-100 Pa exhibited the linear regions for all the bio-oils as noted in Fig. 4. A shear stress of 55 Pa was selected for frequency and temperature sweep. As evident from the figure, the storage modulus (G') was predominant than that of loss modulus irrespective of the feedstocks, whereas Ba et al (2004) observed the loss-modulus as dominant behavior of the bio-oil produced from softwood bark through vacuum pyrolysis. In another study, Garcia-Perez et al (2008) reported that the storage modulus was lower than that of loss modulus for the bio-oil produced from mallee woody biomass. Ba et al (2004) identified four different regions including two plateaus for G' , which was not observed in this study. The bio-oils from corn cob (3 and 4) produced in a batch MAP had a high storage modulus than that of bio-oils from corn cob produced in continuous MAP as evident from Fig. 5. The bio-oil produced from batch MAP (corn cob 3 and 4) had lower loss modulus than the bio-oil from continuous MAP of corn cobs and batch MAP of other feedstocks. The storage and loss moduli were similar for the bio-oils produced from corn cob in a batch MAP with or without catalyst (Fig. 5).

The frequency sweep was conducted in the range of 0.1-100 Hz and found the linear region between 1 and 100 Hz. Accordingly, the frequency sweep experiments were repeated and identified the linear region between 10 and 100 Hz as shown in Fig. 3. As G' approaches a slope of more than 2, which confirms the existence of linear viscoelastic region (Tzanetakis et al., 2008). Similarly, G'' approaches a slope of more than 2 (less than slope of G'), which is also consistent with linear viscoelastic behavior. A frequency of 50 Hz was selected from the linear range depicted in Fig. 4 for temperature sweep. The frequency sweep was also confirmed that the storage modulus was predominant than that of respective loss modulus of each bio-oil. Tzanetakis et al (2008) reported that the loss modulus was ten times higher than that of storage modulus for the bio-oil produced from hardwood, and it was an

opposite observation. Similar to stress sweep, the bio-oil produced from corn cob 3 and 4 in a batch MAP had lower loss modulus than the bio-oil from other feedstocks including corn cob. The storage and loss moduli were overlapping between the bio-oils at a low frequency (10Hz) and a clear difference was observed as frequency increases. The bio-oil from aspen and canola had a higher storage and loss moduli than that of bio-oils from corn cob.

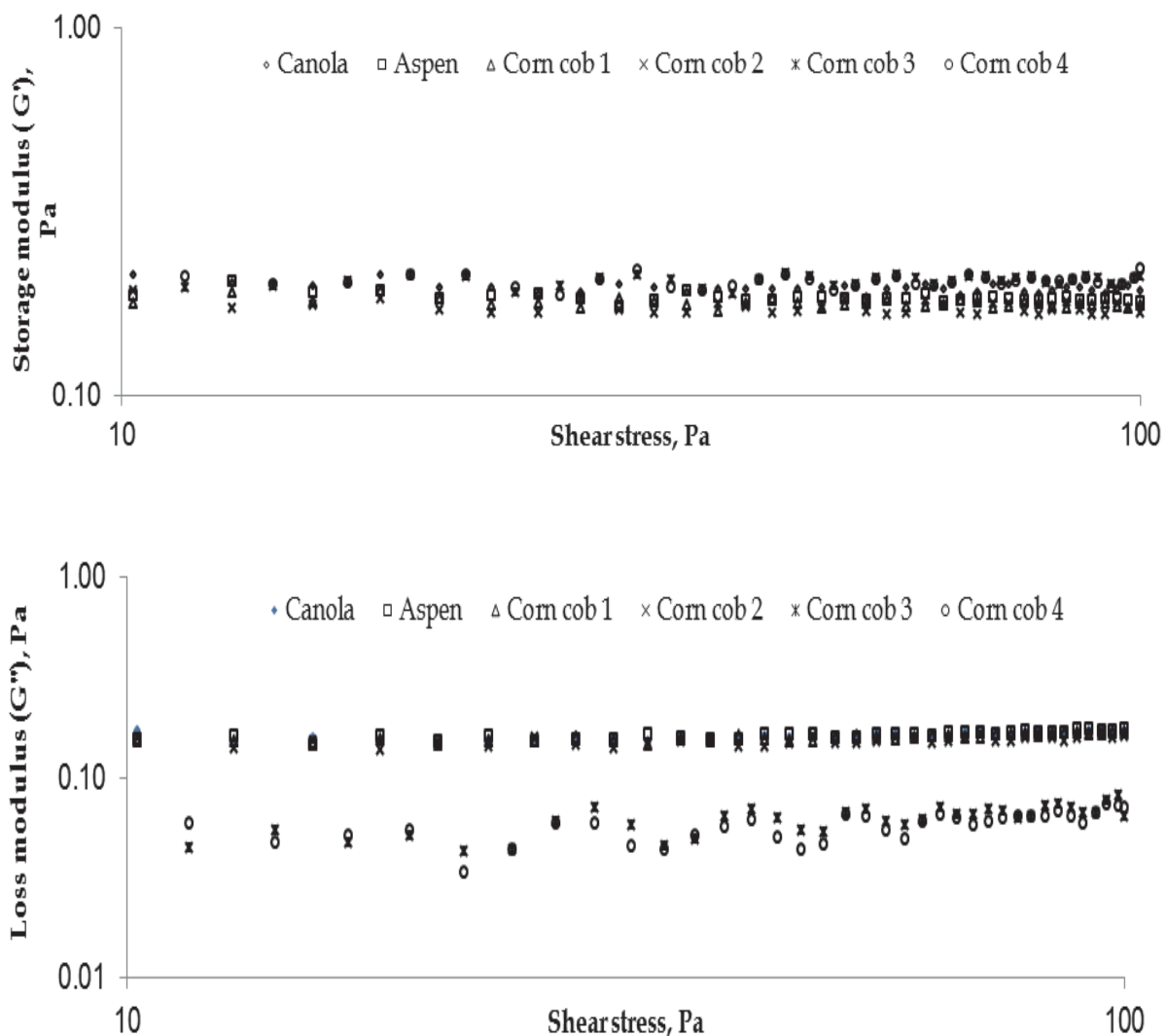


Fig. 4. Stress sweep of bio-oils from produced from different feedstocks

3.5 Temperature sweep

Temperature sweep of the bio-oils were conducted with a shear stress of 55 Pa and a frequency of 50 Hz. The rate of temperature increase was maintained at 10°C/min. The storage and loss moduli trend for all the bio-oils are shown in Fig. 6. The moduli of bio-oil from canola showed a decreasing trend once the temperature reached 80°C. Again, the temperature sweep also confirmed that the storage modulus was more predominant as compared to loss modulus of the bio-oils from different feedstocks. Typically bio-oils are Newtonian fluids (Oasmaa & Peacocke, 2001; Oasmaa et al., 2003); however, in Fig. 6 storage and loss moduli lines confirm that the behavior of bio-oils as non-Newtonian fluids irrespective of the feedstocks.

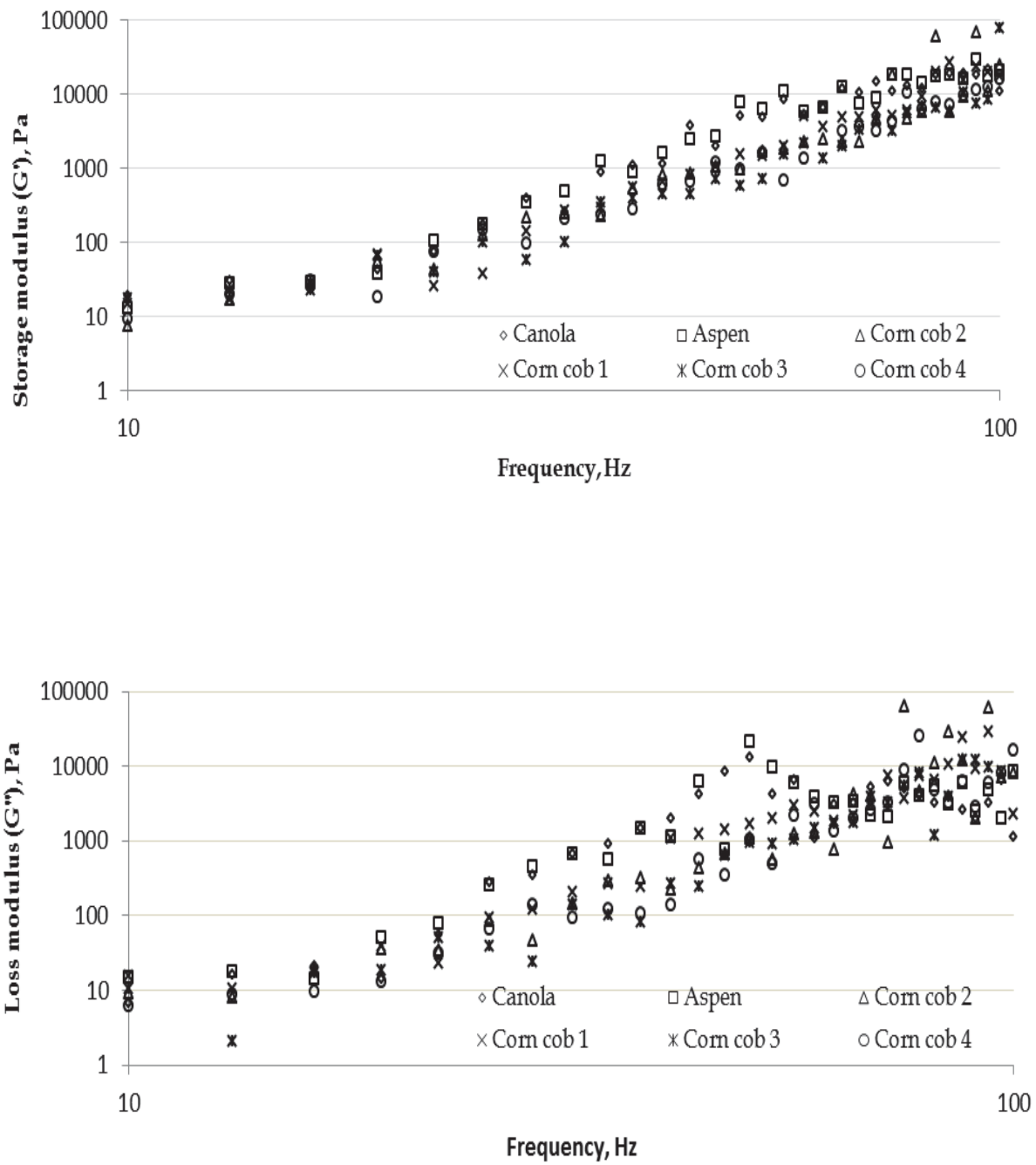


Fig. 5. Frequency sweep of bio-oils from produced from different feedstocks

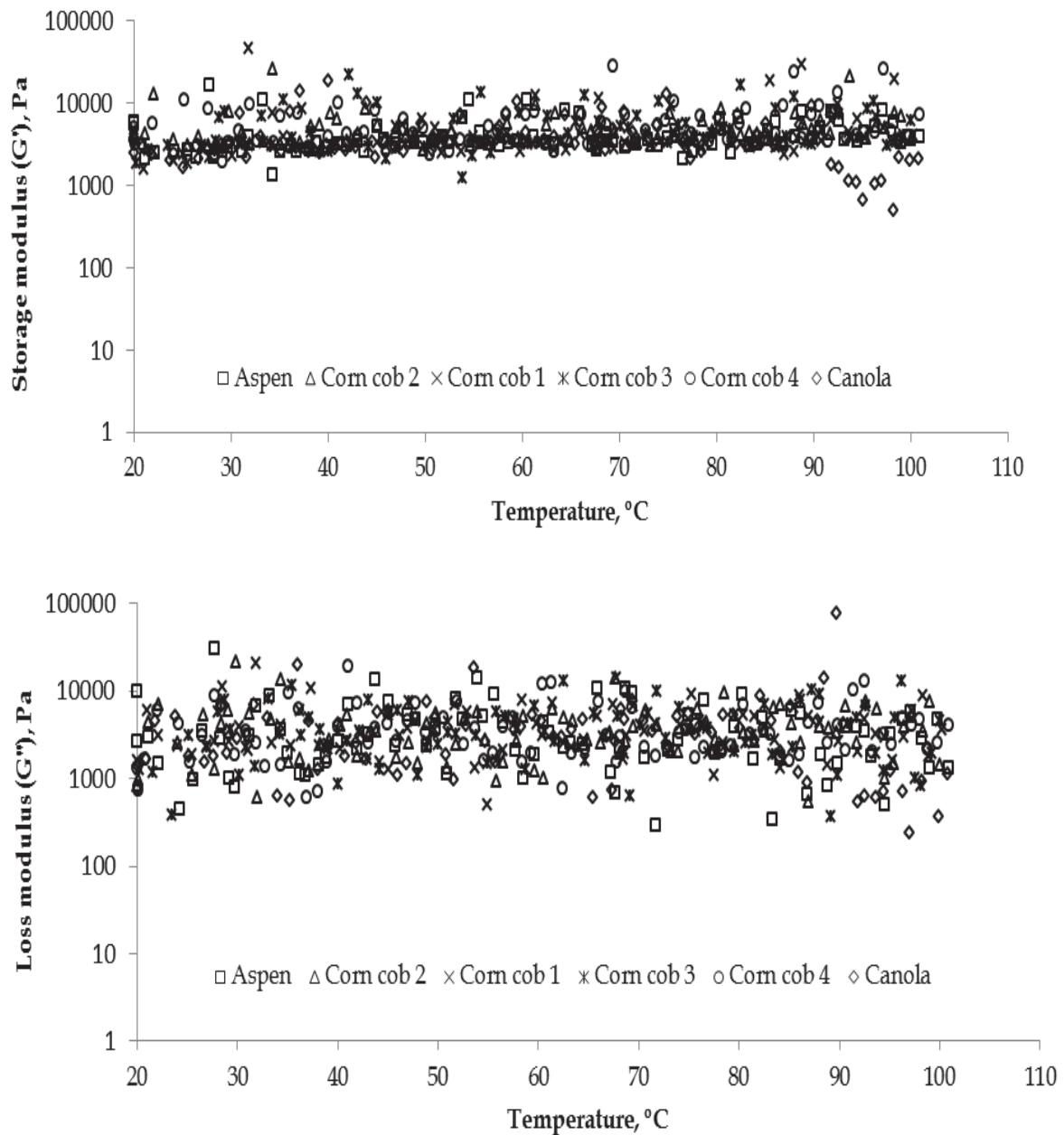


Fig. 6. Temperature sweep of bio-oils produced from different feedstocks

4. Conclusions

When handling bio-oils, viscosity is an important parameter. A thorough rheological characterization was performed on bio-oils produced from aspen, canola, and corn cobs through MAP. Results from simple viscosity and dynamic rheology indicated that the bio-oils tested in this study behaved as non-Newtonian fluids. The viscosities of the bio-oils were in the range of 0.00272 - 0.00196 Pa.s at 20°C and 0.00236 - 0.00163 Pa.s at 40°C. These viscosities are much less than the viscosities of bio-oils derived from different feedstocks reported in the previous literature. Moreover, the bio-oils used in this study had a lower viscosity than that of light and heavy fuel oil, the US #4 fuel oil, and ASTM burner fuel standard indicating varieties of potential application. The viscosity range of the bio-oils

indicates that they are easy to handle and processing; however, viscosity is not the only factor deciding the application of bio-oil. Therefore, other factors should be investigated to assess the suitability of these bio-oils.

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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