RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Physiochemical Characterization of Synthetic Bio-oils Produced from Bio-mass: A Sustainable Source for Construction Bio-adhesives

Shahrzad Hosseinnezhad[a], Ellie H. Fini[b](contact author), Brajendra Kumar,[c] Mufeed Basti[d] and Bidhya Kunwar[e]

[a] Research Assistant, Energy and Environmental Sustainability, North Carolina A&T State University, 1601 E. Market St., Greensboro, NC, 27411, Phone: (336) 334-7737 ext. 665, Fax: (336) 334-7126, shossein@ncat.edu

[b] Associate Professor, Department of Civil Engineering, North Carolina A&T State University, 1601 E. Market St., Greensboro, NC 27411, Phone: (336) 336-28536, Fax: (336) 334-7126, efini@ncat.edu

[c] Senior Research Scientists, Illinois Sustainable Technology Center, Prairie Research Institute, University of Illinois, Urbana-Champaign, 1 Hazelwood Dr. Champaign, IL 61820, bksharma@illinois.edu

[d] Associate Professor, Department of Chemistry, North Carolina A&T State University, 1601 E. Market St., Greensboro, NC 27411, Phone: (336) 336-28536, Fax: (336) 334-7126, basti@ncat.edu

[e]. Post-doctoral Research Associate, Illinois Sustainable Technology Center, Prairie Research Institute University of Illinois, Urbana-Champaign, 1 Hazelwood Dr., Champaign, IL 61820, bkunwar@illinois.edu

ABSTRACT

This paper investigates physicochemical properties of four different types of bio-oil produced through hydrothermal liquefaction (HTL) and vacuum pyrolysis including wood pallet, corn stover, miscanthus and swine manure. It should be noted that the term bio-oil in this paper is used to refer to synthesized oil from post processing of biomass. Accordingly, swine manure was processed under HTL conditions of 340°C, 10–12 MPa with 15 min residence time. Bio-oils from miscanthus, corn stover and wood pellet were produced at 450°C under vacuum pyrolysis. Furthermore, in this paper the merit of applying each of these bio-oils as a precursor for producing bio-adhesive was studied using physiochemical and rheological characterization.

Chemical functional groups and individual compounds were identified with GC-Ms, NMR and FT-IR while molecular weights was determined by GPC showing that wood pellet based bio-oil has the lowest molecular weight followed by those from corn stover, miscanthus and swine manure. In addition, boiling point distributions of different fractions of bio-oils were analyzed. Furthermore, TLC-FID was used to determine different fractions of bio-oils based on their solubility in comparison with those of petroleum. It was shown that overall bio-oils from woody bio-mass have higher amount of alcoholic compounds as evidenced by the presence of strong peaks related to ether and alcohols in FTIR spectra; in addition, the TLC-FID analysis showed presence of higher fraction of fused poly aromatic rings referred to “asphaltene” in bio-oils produced from woody biomass compared to bio-oils from swine manure. The results of our characterization show the importance of feedstock composition and their effect on the characteristics of bio-oils as well as their applicability for use in bio-adhesives production.

Keywords: Bio-oil, bio-adhesives, wood pallet, corn stover, miscanthus and swine manure

INTRODUCTION

Because of the increasing price of petroleum and depletion of these resources, as well as concerns about environmental sustainability as relates to conventional crude oils and fuels, the demand for renewable energy resources is going up (Demirbas and Balat, 2006). Currently most of the energy resources for the US are provided by petroleum fuels. Increasing demands for energy and the petroleum-based products as well as issues associated with greenhouse gases has motivated researchers to find alternative, cost effective, renewable and sustainable energy sources. Considering that bio-oil is derived from non-petroleum based renewable resources such as wood, corn and animal waste, it could be promising future fuel sources (Wierzbicka et al., 2005). Overall biofuels are classified as primary or secondary. Primary biofuels are used in natural form, mostly for heating, cooking or electricity production such as firewood, wood chips and animal waste, etc. Secondary biofuels are produced by processing biomass (Nigam and Singh, 2011).

Dry manure as an example for bio-oil resource is approximately 18% of the total biomass from agricultural lands in the US. The negative environmental impact of animal manure as relates to odors and gaseous emission has drawn more attention for converting them into added value products to be used as partial replacement and complementary resources for petroleum-based products such as bio-oil and construction adhesives. Bio-mass is mainly converted to energy resources via either biochemical or thermochemical methods (Fig 1.) (Cantrell et al., 2008).

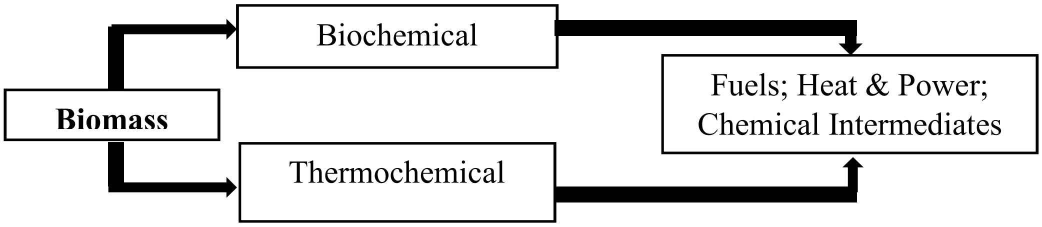

Figure 1. Conversion platforms for livestock waste-to-bioenergy conversion (Cantrell et al., 2008)

Thermochemical process is a physical conversion of biomass by application of high temperatures which leads to breakage of the bonds in organic materials and their subsequent conversion into gas, hydrocarbon fuels, and/or a charcoal residue via a typically fast process which can be completed in seconds or minutes. Thermochemical Conversion (TCC) platform includes combustion, pyrolysis, gasification and liquefaction. In pyrolysis method, heat and a non-oxygen atmosphere are applied to convert the organic portion of a feedstock into a mixture of char and volatile gases which finally form a combustible pyrolysis oil or bio-oil (Cantrell et al., 2008).

To perform the conversion, typically bio-mass is loaded to the reactor and then purged three times with nitrogen to remove oxygen from the environment. After conversion, the reaction mixture consisting of oil, solid, and aqueous solutions are collected for separation. Studies have shown that optimizing pressure and temperature can help increase bio-oil significantly (Fini et al., 2011).

Hydrothermal liquefaction (HTL) is a conversion method for producing liquid fuel from biomass. HTL has been applied to a wide range of feed stocks, including swine manure, cattle manure, microalgae, algae, and sludge (Biller and Ross, 2011; Duan and Savage, 2011; Vardon et al., 2011). During HTL, water plays a role as a reaction medium, reducing the need to dewater biomass which can be a major energy input for biofuel production. Elevated temperature (200–350˚C) and pressure (5–15 MPa) are used to breakdown biomass macromolecules into bio-oil (Zhou et al, 2010).

The research on conversion of biomass is mainly focusing on producing fuels and chemicals (Ozbay et al., 2006; Park et al.,, 2010; Salehi et al.,, 2011). However, some researchers have also been studying the feasibility of bio-mass and resulting bio-oils for use in construction adhesives and asphalt binder (Fini et al. 2011). Airey et al. demonstrated the use of sugars, plant oils, and proteins as alternative sources for producing a synthetic asphalt binder (Airey, 2008). Blends of synthetic and traditional asphalt binder were batched at a ratio of 1:1 and 3:1. Rheological characterization of synthetic bio-binders showed that such raw materials can be fabricated and used to enhance asphalt performance depending on local climates. Seidel and Haddock, studied bio-oils from soy fatty acids (SFA) and showed feasibility of using bio-oils as asphalt modifier (Seidel and Haddock, 2012). While there have been several studies on various bio-oils and bio-binder mechanical and rheological properties for use as construction adhesive, little attention has been given to chemical characterization and comparative studies among variously sourced bio-oils. Therefore, this paper examine and compare the influence of different feed stocks (wood pellet, swine manure, corn stover and miscanthus) on physicochemical characteristics of bio-oil and their applicability for use as a precursor for bio-adhesive production and utilization in asphalt construction.

METHODS

Following sections of the paper elaborates the feedstock resources, bio-oil production processes as well as experimental methods.

Feedstock sources

Swine manure was collected and process at the North Carolina A&T State University's farm while Micanthus, wood pellet and corn stover were collected and converted to bio-oil at the Sustainable Technology Center of the University of Illinois.

Hydrothermal Liquefaction (HTL)

Swine manure was converted into bio-oil under hydrothermal conditions to form a brownish sticky resin referred to as bio-binder (BB) in this paper. Approximately 800g of feedstock adjusted to 20% solid content was loaded into a bio-reactor which is newly developed and manufactured by the authors (Fini et al., 2011); the reactor was then sealed and purged with nitrogen three times to displace headspace gases. The reactor was heated up to 340°C temperature and pressure of 10.3 MP, the reactant medium was maintained at a constant temperature and pressure for 15 minutes. After completion of reaction, liquid medium was rapidly cooled down to the room temperature using a recycled ice-water cooling coil. Following that the gas was released from the autoclave to reduce the pressure in the autoclave to atmospheric pressure. The oil residue was separated from the aqueous solutions by filtration under a vacuum to acquire bio-binder.

Vacuum Pyrolysis

In order to convert Miscanthus (MS), Corn Stover (CS), and Wood Pellets (WP), we used a fast pyrolysis technique. To do so, 3500 grams of each of MS, CS and WP pellets were filled into the reactor to 3/4 of its volume. Before the reactor was placed in the furnace, sealant was applied to avoid leakage during pyrolysis and the vessel was closed tightly. The reactor was then placed in the heating furnace and pipes were connected tightly to avoid bio-oil vapors escaping. The furnace containing pyrolysis reactor was heated to 450°C at a rate of 7°C/min. Liquid fraction (bio-oil) was collected by condensing bio-oil vapors in ice-cooled Erlenmeyer flask. Reaction progress was tracked by monitoring the bubbles of un-condensable gas (captured in a secondary graduated cylinder containing water) exiting the reactor. The graduated cylinder with water was placed next to the flasks and a tube from the Erlenmeyer flasks was connected into the cylinder making sure it is submerged in water to check if there were any bubbles coming out while the process was in progress. The reduction of bubbling to no bubbling indicated that the process was completed.

The non-aqueous liquid fraction was extracted into dichloromethane (DCM) solvent using a separatory funnel. Deionized water (>18 MX) was added to the funnel to form a bi-layer, and the DCM-soluble portion was vacuum filtered using filter paper (Whatman No. 44 ashless filter paper) to remove particulate matter. The DCM was then removed under a nitrogen stream at 40°C.

Chemical Characterization of Bio-oils

The ash content of the bio-oils was determined using Thermogravimetric Analysis using SDT-Q600. The pH of the bio-oils was measured using a digital pH meter (Accumet model 8250, Fisher Scientific). The elemental ratio (C/H/N/O) of the samples was determined using an Exeter Analytical CE-440 Elemental Analyzer at 25°C. Higher heating value (HHV; MJ/kg) was estimated using Dulong's formula (Savage, 2011) using Equation 1:

$$\mathbf{HHV = 0.3383C + 1.422\,(H - O/8)} \qquad \textbf{Equation 1}$$

In which C, H, and O are the mass percentages of carbon, hydrogen and oxygen, respectively.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)

A FTIR spectrometer, Shimadzu, 1.30(2005) single reflection zinc selenide prism was used in absorbance mode to acquire the spectra of bio-oils in wave-numbers ranging from 500cm^{-1} to 4000cm^{-1}. The internal energy levels of a molecule can be divided in three categories, rotational, vibrational and electronic energy levels. In infrared spectroscopy, the interactions between molecule and electromagnetic (EM) fields in the IR region are studied. In this spectral region, the EM waves mainly couple with the molecular vibrations. Therefore, a molecule can be excited to a higher vibrational state by absorbing IR radiation (Sawant, 2011).

For ATR-FTIR, the spectra are obtained by placing a thin layer of sample against a pre-heated internal reflection element. In this method, total internal reflectance of infrared light in a non-absorbing prism is used. Contact of absorbing substances with the prism surface will attenuate the internally reflected light and provides an infrared absorption spectra, corresponding to a spectra recorded of the light passed through the surface layer of the material studied (Karlsson et al., 2006). In this study a sample of each of the bio-modified binders were analyzed to provide a better understanding of the function groups present in each bio-oil.

Thin-layer Chromatography with Flame Ionization Detection (TLC-FID)

To further analyze saturates, aromatics, resins and asphaltenes (SARA) content of each bio-oil an Iatroscan MK-6s model TLC-FID analyzer was utilized. The hydrogen and airflow rate were set to 160 mL/min and 2 L/min, respectively. 1µL sample solution (20 mg/ml in chloroform) was spotted on the chromrods. Chloroform, n-Heptane, toluene and tetrahydrofuran (THF) from Sigma Aldrich were used for solvent development in separate tanks and one tank containing sodium nitrite for humidification. The chromrod frame is placed in the solvent reservoir inside the tank for development while 50 mL of solvent was added to a smaller tank. Dried chromrods were humidified in a sodium nitrite tank and chromrods were then developed in n-heptane tank for 27 min. After the development, rods were dried in the oven at 70°C followed by humidifying for 10 minutes. The same development procedure was used for toluene and THF with development time of 15 and 5 minutes, respectively; finally prepared specimen was scanned for 30s utilizing an Iatroscan containing FID detector.

Gel Permeation Chromatography (GPC)

The Size Exclusion Chromatography analysis was conducted using a Waters 2414 RI detector; Styragel HR1 SEC column (7.8mm × 300mm), Waters 600-MS System controller was connected to a 600-mulitsolvent delivery system, and 717-plus auto-sampler was connected to a Dionex U120 Universal Interface.

Samples (3% w/w in Tetrahydrofuran, THF) were filtered using 0.45-µm Millipore PTFE to remove suspended particulates; a pump flow rate of 1.0 mL/min with THF as the carrier solvent and injection volumes of 50 µL were used. The separation of multi-component mixture took place in the column. A constant flow of fresh eluent was supplied to the column via a pump to detect analytes. It should be noted that GPC separates analytes according to their size. The resulting chromatographic data was processed using Matlab through Equation 2 and 3. The number-average molecular weight (Mn) and weight-average molecular weight (Mw) were calculated based on the component molecular weights (M_i) determined from the retention time calibration curve and signal intensities (N_i).

$$M_n = \frac{\Sigma M_i N_i}{\Sigma N_i}$$ **Equation 2**

$$M_w = \frac{\Sigma M_i^2 N_i}{\Sigma M_i N_i}$$ **Equation 3**

Simulated Distillations (Sim-Dist.) Analysis

Simulated distillation is used mainly to characterize petroleum fractions because it allows quick determination of their boiling range distribution. Here, we used simulated distillations to determine fractions of bio-oils following ASTM-7169-05 method using a HP 5890 Series II FID gas chromatograph and a Durabond DB-HT-SimDis GC column by Agilent-JandW Scientific (5 m × 0.53 mm id, 0.15 µm film). It should be noted that the boiling point–retention time relationship is influenced by chemical structure and heteroatom content. Therefore, the Sim-Dist analysis of bio-oil samples can only be approximated since the heteroatom contents of the bio-oil volatile components are very different from the mixture of the reference compounds used for calibration.

Gas Chromatography–Mass Spectroscopy (GC–MS)

To conduct GC-MS, separation was achieved with a Varian VF-5 ms phenyl–methyl GC column (30 m × 0.25 mm id, 1.0-lm film) using He carrier gas with flow rate of 1 mL/min. One microlitre of DCM extracts (2 wt.% bio-oil) were injected at 270 °C with a split ratio of 30:1. Individual low molecular weight products were identified by matching fragmentation patterns against a NIST database.

^{1}H NMR and ^{13}C NMR Analysis

^{1}H NMR spectra were collected using a Varian Unity 400-MHz spectrometer outfitted with a 5-mm broadband probe. Samples (2.5% w/w) were prepared by dissolving 50–75 mg of bio- oil in deuterated chloroform containing 0.03% tetramethylsilane (TMS) as an internal reference. Samples were then filtered (0.45- lm PTFE) to remove any suspended particulates before loading into 5 mm diameter NMR tubes. ^{13}C NMR spectra were collected using a Varian Unity 600-MHz spectrometer outfitted with a 10-mm broadband probe. Samples were prepared at concentration of 7–10% (w/w) in deuterated chloroform with 0.03% TMS and filtered (0.45 μm PTFE) before loading into 10 mm diameter NMR tubes. NMR spectra were processed and integrated with Mnova software according to functional group associated for ^{1}H and ^{13}C NMR peaks. The signal areas for trace protons from deuterated chloroform (7.26 ppm for ^{1}H NMR; 77 ppm for ^{13}C NMR) were excluded during spectrum integration.

Rheological Characterization of Bio-oils

To further understand physical and mechanical properties of bio-oils, the rheological and surface properties of each bio-oil were studied using several methods as explained below.

Dynamic Shear Rheometer (DSR)

To study the stress- strain relation in each bio-oil a Thermo Scientific HAAKE MARS III Rheometer was used in strain sweep mode. To evaluate the elastic and viscous component of bio-oils, samples of 0.25 mm thickness were cast between the two parallel plates of stainless steel with 35mm in diameter. The test was performed by applying a strain sweep test at temperatures ranging from 20ºC to 50ºC.

Surface Tension

The surface tension (also known as interfacial tension) of a liquid is defined as work required for increasing the surface size of the liquid. It has been shown that a decrease in surface tension could lead to an improved wettability (Speight, 2014). Therefore, the surface tension test was conducted to evaluate wettability characteristics of each bio-oil. To do so, a Drop Shape Analyzer (DSA-100 model) made by Kruss using the Pendant Drop method was utilized to determine in air surface tension of the samples. This instrument takes an image of the drop with the use of a high speed camera which is then analyzed by the software to generate a geometrical model to best fit the contour of the drop.

DATA ANALYSIS AND DISCUSSION

The results of aforementioned experiments showed significant variation between bio-oils while plant based bio-oils showed some similarity in their properties, they differ significantly from those produced from processing of animal manure. Overall, analyzing physiochemical properties of bio-oils showed that pH value of wood based bio-oils is less than bio-oil from swine manure (Table 1). Most of the bio-oils are acidic due to the presence of organic acids like formic and acetic acid. However, in the case of swine manure-based bio-binder (BB), the higher nitrogen content gave rise to the basic properties and increase of the pH value. In addition, it was found that heating value of bio-oils was highest for BB followed by MS, CS and WP. Furthermore, Elemental analysis showed that BB has the highest nitrogen content which could be attributed to the high amount of proteins in the feedstock compared to those of wood based resources. However, in contrast, WP showed to have the highest amount of oxygen which relates to presence of high fractions of carbohydrates which was in agreement with prior work by Biller and Ross, 2011.

Table 1. Physiochemical Properties of Bio-oils

Bio-oil	pH	Density (g/ml)	Higher Heating Value (MJ/Kg)	Elemental Composition (wt%)				Ash Content (wt%)
				C	H	N	O	
BB	5.97	0.96	29	63.44	8.36	3.53	24.38	10.34
WP	2.80	1.23	25	61.05	6.93	0.21	31.81	6.84
CS	2.87	1.25	26	61.6	7.28	0.96	30.16	9.27
MS	2.95	1.05	28	65.77	7.31	0.67	26.25	2.14

Characterization of molecular structure using FTIR-ATR showed that all bio-oils derived from wood based materials have similar aromatic and aliphatic functional groups. However, animal based bio-binder found to be significantly different (Figure 2). Table 2 shows the chemical groups associated with bio-oils and their corresponding wave numbers.

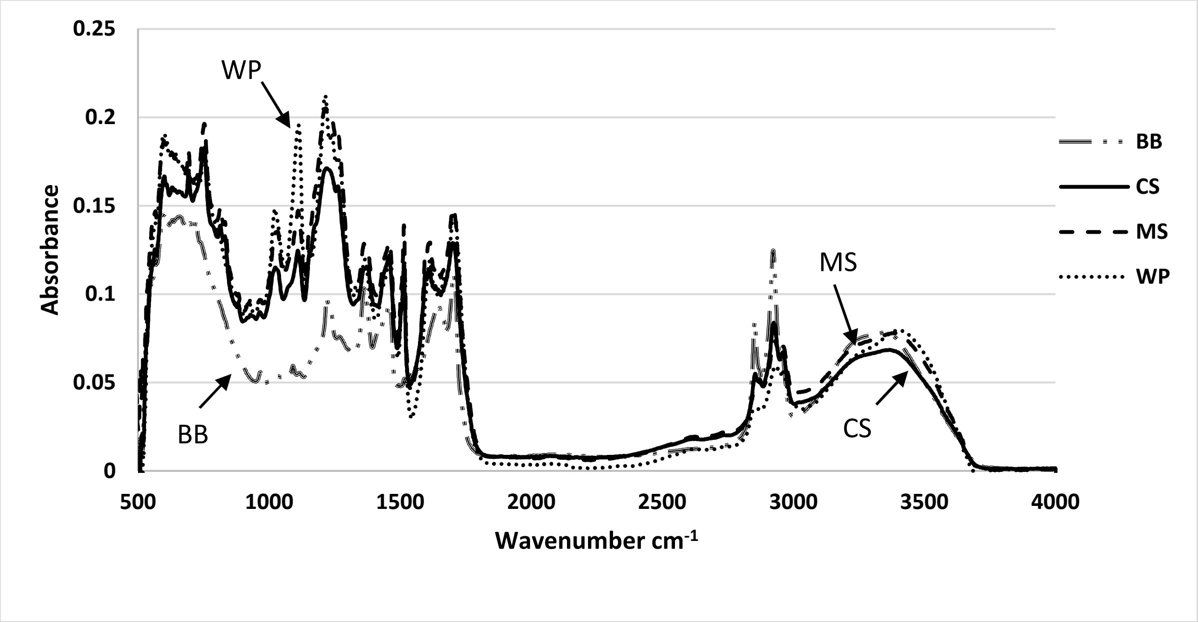

Figure 2. FT-IR Spectra of Bio-oil Samples

Table 2. Functional Group for MS, CS, and WP

Wavenumber (cm^{-1})	**Functional Group**
3400-3200	-OH stretching
3000-2800	Aliphatic CH stretching
1700-1710	Aromatic carbonyl/carboxyl C=O stretching
1514-1560	Aromatic C=C ring stretching
1454	Aliphatic CH deformation
1370	Aliphatic CH_3 deformation
1250-1270	Aromatic CO– and phenolic –OH stretching
1010-1014	Ether or alcohol C-O stretching
770-780	Aliphatic CH deformation

As it can be seen in Figure 2, BB has very different functional groups; this can be attributed to highly different chemical structure of its bio-mass feedstock. Two sharp peaks around 1800-1900 cm^{-1} in BB spectra indicate presence of aliphatic groups. Similar to elemental analysis, the high carbon and hydrogen content of BB showed prominent C-H stretch (3000–2840 cm^{-1}). Comparison of BB with wood based bio-oils can help explain some of the variations observed in their different susceptibility to oxidative aging. Accordingly, their prominent difference is related to the extent of ether and alcohols (1020cm^{-1}) which appear to be much higher in wood based bio-oils making them to be more susceptible to oxidative aging compared to those from swine manure.

To further investigate applicability of bio-oils as a precursor for bio-adhesive production and for use as modifiers in asphalt binder, various fractions of bio-oils were also compared with those of typically used control asphalt. The results of TLC-FID analysis of bio-oils show that asphaltene content in MS is the highest among all bio-oils followed by CS, WP and BB. It should be noted that Peterson and his group has documented relative oxidation susceptibility of asphalt components to be the highest for asphaltenes (40%) followed by polar aromatics (32%), with naphthene aromatics and saturates showing the least reactivity of 7% and 1%, respectively. Accordingly, the presence of higher amount of asphaltene in MS could indicate higher oxidation rate for MS, while BB with the least asphaltene could result in the lowest propensity to oxidation when added to asphalt. These findings showed to be in agreement with previous studies showing that introduction of MS to asphalt binder increased the oxidation susceptibility of the base asphalt (Fini et al., 2015).

Further comparing TLC-FID results between bio-oils and the control asphalt showed that bio-oils has overall higher resin and asphaltene content then the control asphalt while their aromatic content is relatively lower than asphalt.

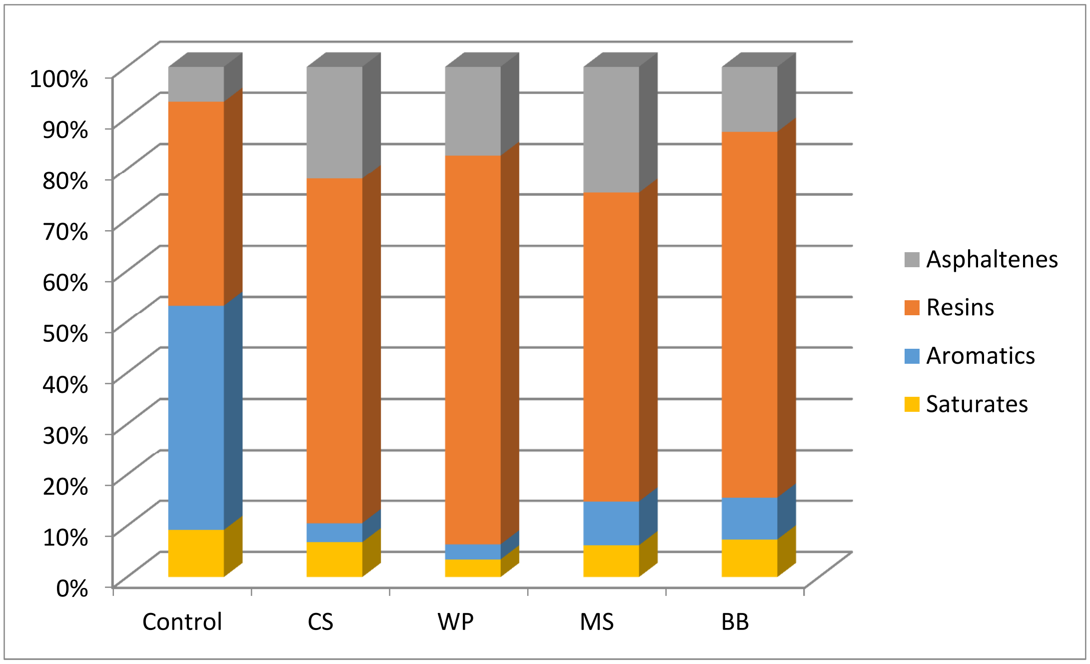

Figure 3. TLC-FID Results for Bio-oils

Since bio-oils contain different components such as water and phenolic compounds their average molecular weight is highly different depending on their bio-mass resources. It should be noted that molecular weight is strongly related to physical properties such as volatility and viscosity of the bio-oils. As it can be seen in Table 3, BB has the highest molecular weight followed by MS, CS and WP. This is in agreement with significantly higher viscosity values measured for BB compared to the three plant based bio-oils.

Table 1.Molecular Weight for Bio-oils

Name of Bio-oil	Mn	Mw
CS	137	960
MS	192	1035
WP	192	610
BB	1011	2978

Study of boiling point distribution of bio-oils showed that they are mostly within the range of heavy vacuum gas oil (343–538 °C) (Figure 4). Corn Stover had the highest percentage (35%) of low boiling point compounds (bp < 190 °C), corresponding to heavy naphtha. In contrast, Bio-oil from swine manure had the highest percentage (10%) of high boiling point compounds (bp > 538 °C), corresponding to vacuum residue. Also, Swine manure bio-oil had the highest percentage (63%) of mid-boiling point compounds (bp 343–538 °C) and the lowest percentage of naphtha and kerosene. This order is in agreement with the aforementioned weight average molecular weights (MWw). Based on these results, bio-oils studied in this paper can be promising candidates for use in asphalt due to their significant similarity to vacuum gas oil and vacuum residue fractions from petroleum crude oil. In addition, it was found that among these four bio-oils, BB has more potential for application as an adhesive mainly because it has higher percentage of heavy content as classified by vacuum gas oil and vacuum residue with boiling point of higher than 343ºC and shows the lowest propensity for oxidation.

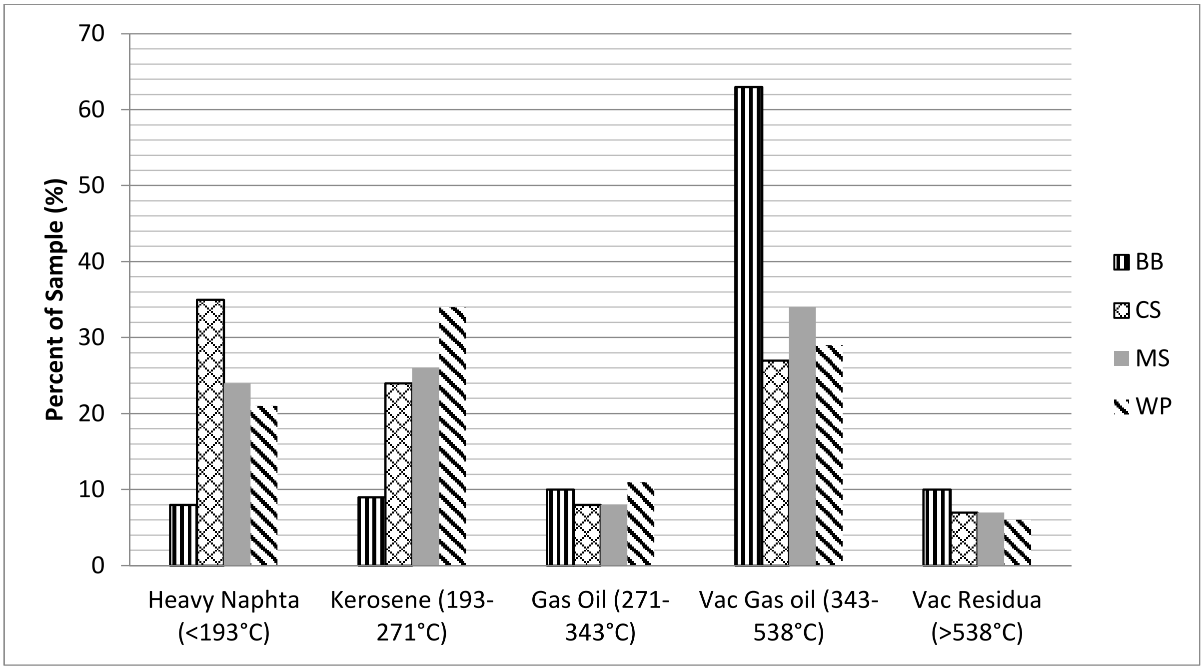

Figure 4. Sim-Dist Boiling point Fractions of Bio-oils

To further examine functional groups for each bio-oil, NMR analysis was performed. The study results were in agreement with those of FTIR analysis. In the ^{1}H NMR spectra, region from 0-3 ppm is the characteristic of aliphatic hydrogen atoms which can be divided into two sub-regions of alkanes and unsaturated. Figure 5 shows the highest percentage of alkane functional groups (0.5–1.5 ppm) for BB in comparison to other bio-oils. This could be attributed to the decomposition of fatty acids in swine manure under hydrothermal conditions resulting in high percentage of alkane groups. On the other hand, WP exhibited the lowest alkane functionality but the highest percentage of unsaturated functionality (1.5–3.0 ppm), this can be related to higher nitrogen and oxygen compounds which is in agreement with prior study by Zhou et al., 2010. Low percentage of carbohydrate at (4.4– 6.0 ppm) for all bio-oils indicates that carbohydrates of wood based bio-mass and animal waste bio-mass were converted to bio-oil; this is in agreement with prior work by Duan and Savage, 2011. Aromatic/ hetero-aromatic functionality was also observed for all bio-oils (6.0–8.5 ppm).

The 13C NMR spectra provide more detail signals in different regions. The region from (0-55 ppm) attributed to high aliphatic content (0–55 ppm) which has been observed for all bio-oils in the integrated peak area regions (Figure 6). Aliphatic compounds were further divided into short (0– 28 ppm) and long branched (28–55 ppm); analyzing each category showed that BB has the highest percentage of short branched and WP has the highest portion of long-branched aliphatic compounds.

Also ^{13}C NMR spectra confirmed presence of aromatic and olefin carbons in all bio-oils. Low percentages of alcohol/ ethers/carbohydrates (55–95 ppm) were also observed in all ^{13}C NMR spectra, which is another confirmation of successful conversion of carbohydrates in the feedstock to bio-oils.

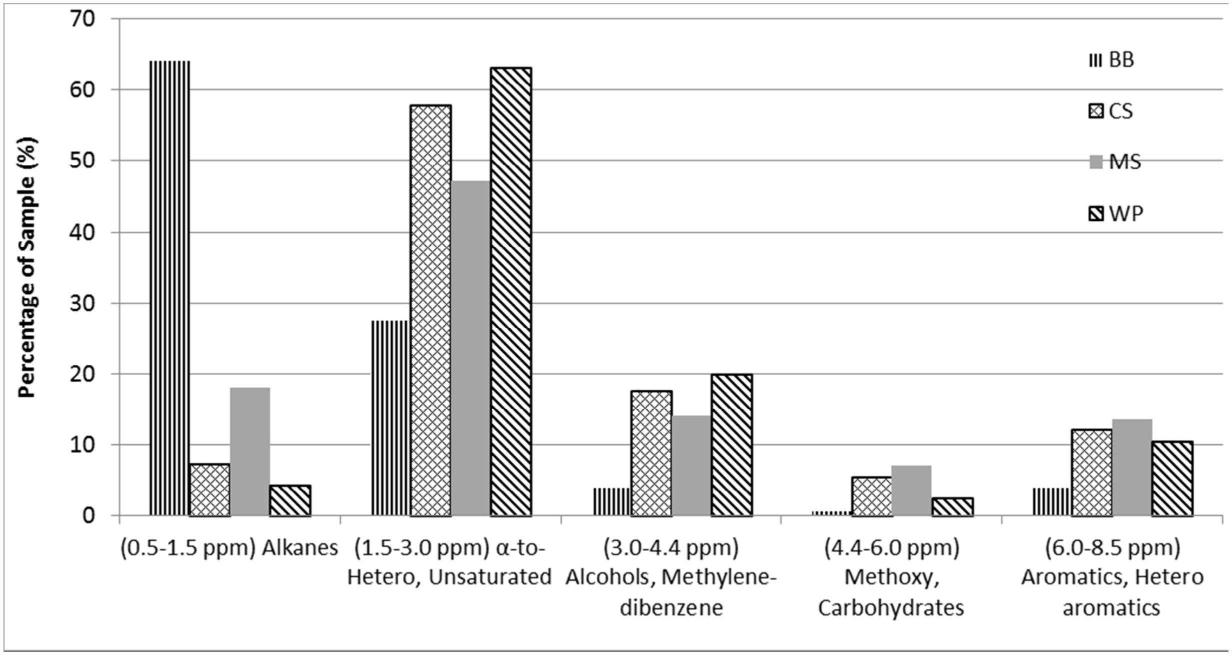

Figure 5.^{1}H NMR Spectral of bio-oils Based on Integrated Peak Areas

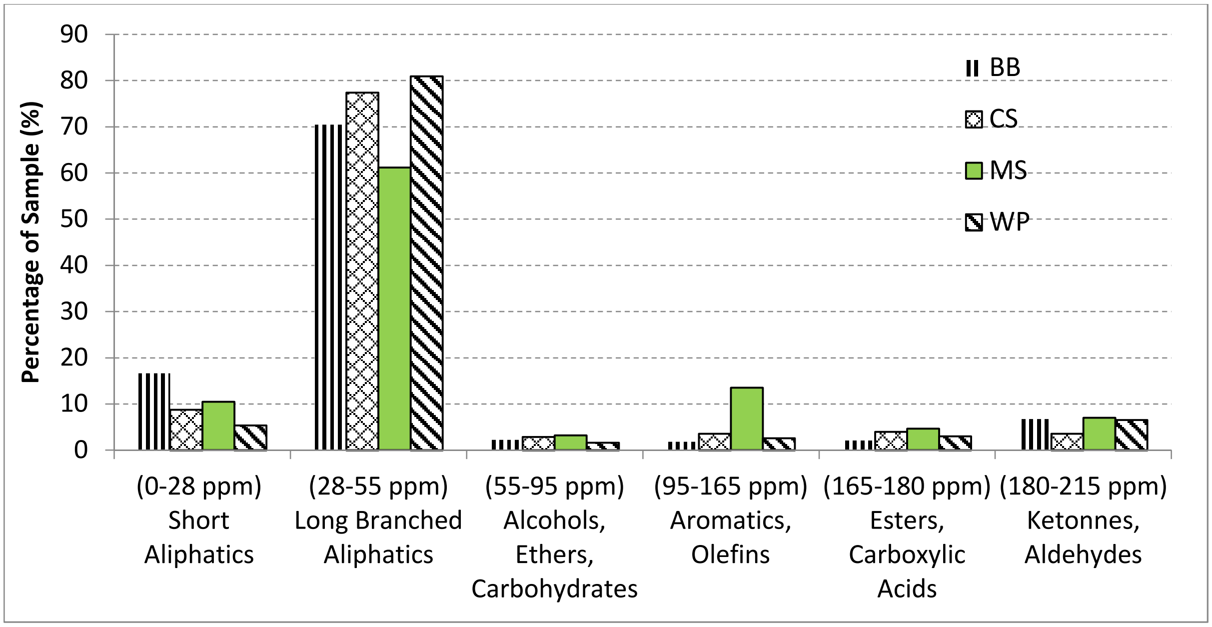

Figure 6. ^{13}*C NMR Spectral of Bio-oils Based on Integrated Peak Areas*

GC-MS analysis for the bio-oils was performed to study the diversity of components of different feed stocks bio-oils. The peaks of the chromatogram were matched with NIST library to identify the compounds. Components which were identified derived from lipid, proteins, cellulose, and lignin. Nitrogen derived compound were from proteins decomposition and lignin decomposition resulted in phenolic component, aldehydes, furan, ketones, and oxygenates compounds were derived from cellulose (Mullen and Boateng, 2008). Table 4 shows some identified compounds for four bio-oils.

To further study the rheological and surface characteristics of each bio-oil, stress developed during a strain sweep test was monitored (Figure 7). It can be seen that the stress build up with the increase in percentage of strain is the highest for CS followed by WP, BB and MS. At 50% strain level, the stress measured in CS, WP, BB and MS found to be 223.56, 131.13, 149.95 and 43.34 Pa, respectively.

Table 4. Bio-oil Compounds Detected from GC-MS Chromatogram

No.	**CS**	**BB**	**WP**	**MS**
1	4-(3-Hydroxy-2,2,6-trimethyl-7oxa-bicyclo[4.1.0]hept-1-y)-but-3-en-2-one	10-(Mthoxycarbonyl)-N-acetylcolchinol	Ingol 12-acetate	10-(Methoxycarbonyl)-N-acetylcochinol
2	Conessine	Heptadecanenitrile	4-(3-Hydroxy- 2,6,6-trimethyl cyclohex-1-enyl)pent-3-	4-H-Benzopyran-4-one, 2-(2,6-dimethoxyphenyl)-5,6-dimethoxy-
3	10-Methyl-8-tetradecan-1-ol acetate	Benzo[c]cinnolin-4-amine, N,N-dimethyl-	(7a-Isopropenyl-4,5-dimethyloctahydroinden-4-yl)methanol	N-Carboxylethyl colchiceine
4	Propanoic acid, 2-(3 acetoxy-4,4,14-trimethylandrost-8-en-17-yl)	Nandrolone decanoate	Methenolone	Propanoic acid, 2-(3 acetoxy-4,4,14-trimethylandrost-8-en-17-yl)
5	4H-1-benzopyran-4-one, 2-(3,4-dimethoxyphenyl)-3,7-dimethoxy	Benz[c]acridine, 1,2,3,4,8,9,10,11-octahydro-7-methyl-	E-10, 13, 13-Trimethyl-11-tetradecen-1-ol acetate	3-Butan-2-ol, 2-methyl-4-(1,3,3-trimethyl-7-oxabicyclo[4.1.0]hept-2-yl)-
6	2H-1-Benzopyran-3-carboxylic acid, 2-ethoxy-2,4-diphenyl-, ethyl ester	Methanone, phenyl(5,6,7,8-tetrahydro-1-naphthalenyl)-	Cyclohexane, 1,4-dimethyl-2-octadecyl-	2H-1-Benzopyran-3-carboxylic acid, 2-ethoxy-2,4-diphenyl-, ethyl ester
7	Hexadecanoic acid, (2-pentadecyl-1,3-doxolan-4-yl)methyl ester	Bufa-20,22-dienolide, 3,14-dihyroxy- (3β, 5 β)-	7-(2-Hydroxy-1-methylethyl)-1, 4a-dimethyldecahydronaphthalen-2-ol	4-(3-Hydroxy-2,6,6-trimethylcyclohex-1-enyl)pent-3-en-2-on
8	3-Buten-2one, 3-methyl-4-(1,3,3-trimethyl-7-oxabicyclo[4.1.0]heptan-1-yl)	2-Oxo-4, 6-diphenyl-3-(4-tolyl)-1,2,3,4-tetrahydropyrimidine	Acetic acid	Acetic acid
9	Cholestan-3-one, cyclic 1,2 ethanediyl aetal	2-Oxazoline, 4,4-dimethyl-2-(heptadec-7-enyl)-,(E)	4-(3-Hydroxy-2,6,6-trimethylcyclohex-1-enyl)pent-3-en-2-one	Cyclohexane, 1,1-(2-propyl-1,3-propanediyl)bis-
10	Cyclohexane, 1,4-dimethyl-2-octadecyl-	(17α)-3-Methoxyestra-1,3,5(10)-trien-17-ol	Spiro[4.5]decan-7-one, 1,8-dimethyl-8,9-epoxy-4-isopropyl-	10-Methyl-8-tetradecan-1-ol acetate

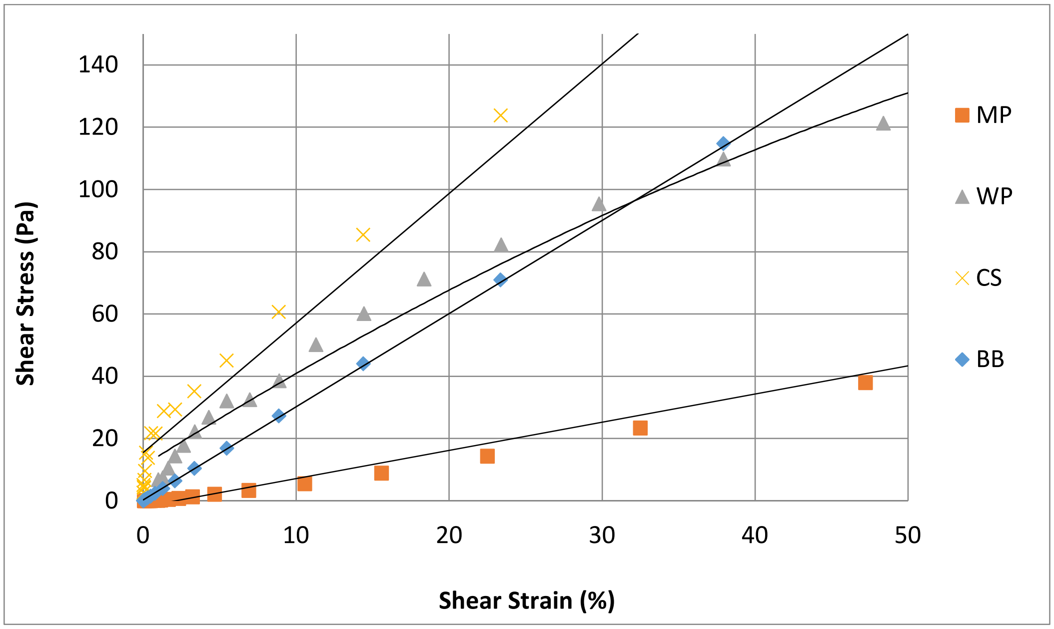

Figure 7. Shear Stress based on Applied Strain for Bio-oils

Furthermore, surface tension analysis was conducted to evaluate each bio-oils wettability properties. Commonly, surface tension is used as an indicator of the energy required to increase the size of the surface of a selected substance/liquid. It has been shown that liquids with low surface tension could have improved wettability characteristics leading to better adhesion properties. As it can be seen in Figure 8, surface tension value was the highest for BB followed by MS, CS and WP. This in turn, could indicate that WP has the highest ability to wet the surfaces and promote adhesion. Also, the results of surface tension for bio-oils were in agreement with values previously reported in the literature (Garcia-Perez, 2006).

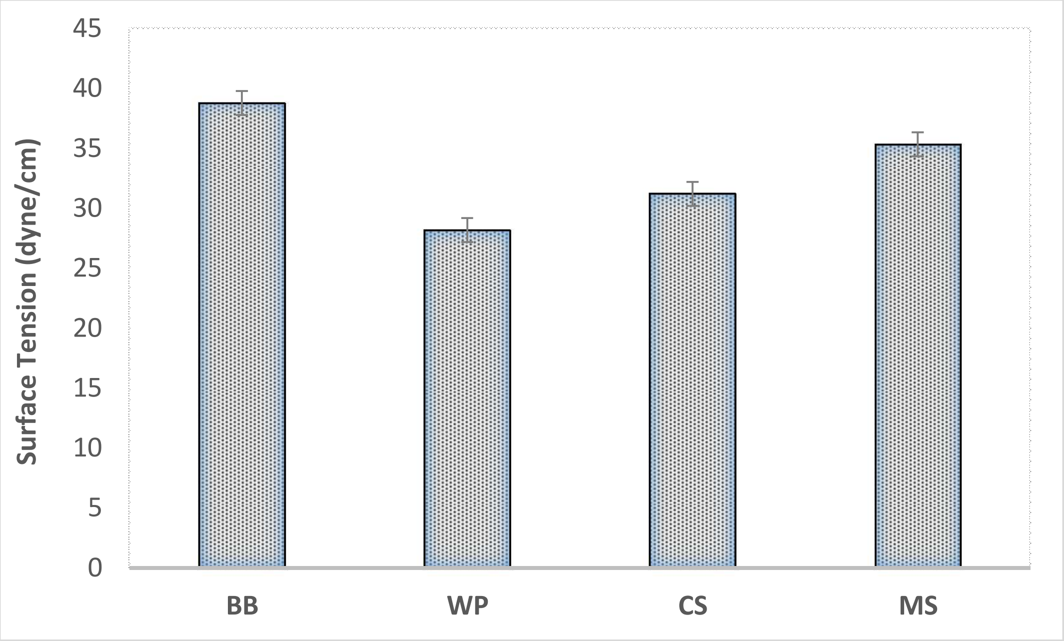

Figure 8. Surface Tension for All Bio-oils

SUMMARY AND CONCLUSION

This paper investigates physicochemical properties of four different types of bio-oil produced through hydrothermal liquefaction (HTL) and vacuum pyrolysis to evaluate their applicability for use as modifiers and/or precursor for production of bio-adhesives. The study involves chemical, rheological and surface characterization of each bio-oil. It was shown that overall bio-oils from woody bio-mass have higher amount of alcoholic compounds as evidenced by the presence of strong peaks related to ether and alcohols at (1020 cm-1); in addition, the TLC-FID analysis showed presence of higher fraction of fused poly aromatic rings referred to "asphaltene" in bio-oils produced from woody biomass compared to that of swine manure with miscanthus having the highest asphaltene content among all samples in this study. Considering that asphaltenes are known to be highly susceptible to oxidation, this further confirms previous studies showing that introduction of miscanthus based bio-oils to asphalt binder increased the oxidation susceptibility of the base asphalt (Fini et al., 2015). In addition, comparative analysis among four bio-oils showed that bio-oil from swine manure has the highest percentage of heavy content as classified by vacuum gas oil and vacuum residue with boiling point of higher than 343ºC.

With regard to rheological properties, it was found that the stress build up with the increase in strain is the highest for CS followed by WP, BB and MS. In terms of their surface characteristics, wood based bio-oil found to have the lowest surface tension followed by CS, MS and BB indicating better wettability characteristics in WP. The results of our characterization showed the importance of feedstock composition and their effect on the characteristics of bio-oils as well as their applicability for use in asphalt. Providing a better understanding of physiochemical properties of both plant-based and manure based bio-oils, this paper contributes to the design and engineering of renewable and durable construction bio-adhesives from bio-mass. This in turn, can not only address the global issue related to diminishing petroleum resources but also offer an economically viable venue to sequester biomass carbon which otherwise will be released to atmosphere as bio-mass decay.

ACKNOWLEDGEMENT

This research is sponsored by the National Science Foundation (Award No: 1150695). The authors would like to acknowledge the invaluable assistance provided by Ahmed Lammare of North Carolina A & T State University. The contents of this paper reflect the view of the authors, who are responsible for the facts and the accuracy of the data presented. This paper does not constitute a standard, specification, or regulation.

References:

Airey, G., Mohammed, M., and Fichter, C. (2008). Rheological Characteristics of Synthestic Road Binders. *Fuel, 87*(10-11), 1763-1775.

Biller, P., and Ross, A. B. (2011). Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. *Bioresour Technol, 102*(1), 215-225. doi: 10.1016/j.biortech.2010.06.028

Cantrell, K. B., Ducey, T., Ro, K. S., and Hunt, P. G. (2008). Livestock waste-to-bioenergy generation opportunities. *Bioresource Technology, 99*, 7941–7953. doi: 10.1016/j.biortech.2008.02.061

Demirbas, M. F., and Balat, M. (2006). Recent advances on the production and utilization trends of bio-fuels: A global perspective. *Energy Conversion and Management, 47*(15-16), 2371-2381. doi: 10.1016/j.enconman.2005.11.014

Duan, P., and Savage, P. E. (2011). Upgrading of crude algal bio-oil in supercritical water. *Bioresour Technol, 102*(2), 1899-1906. doi: 10.1016/j.biortech.2010.08.013

Durange, J. A. C., Santos, M. R. L., Pereira, M. M., Fernandes Jr, L. A. P., Souza, M. N., Mendes, A. N.,Carvalho, N. M. F. (2013). Physicochemical Properties of Pyrolysis Bio-Oil from Sugarcane Straw and Sugarcane in Natura. *Journal of Biomaterials and Nanobiotechnology, 04*(02), 10-19. doi: 10.4236/jbnb.2013.42A002

Fini, E., Oldhoms,D., Hosseinnezhad, S., Buabeng, F. (2015). *Investigating the Aging Susceptibility of Bio-Modified Asphalts*. Paper presented at the International Airfireld and Highway Pavemnets Conference, Miami, FL , June 7-9, 2015.

Fini, E., Al-Qadi, I., Y., Zada, B., Mills-Beale, J. (2011). Partial replacement of asphalt binder with bio-binder: characterisation and modification. *International Journal of Pavement Engineering*, 6(13), 515-522. doi: 10.1080/10298436.2011.596937

Karlsson, R., Isacsson, U., and Ekblad, J. (2006). Rheological characterisation of bitumen diffusion. *Journal of Materials Science, 42*(1), 101-108. doi: 10.1007/s10853-006-1047-y

Garcia-Perez. M, A. Chaala, H. Pakdel, D. Kretschmer, D. Rodrigue, and C. Roy, (2006), Multiphase Structure of Bio-oils, *Energy and Fuels,* 20, 364-375

Mullen, C., and A. Boateng, (2008), Chemical Composition of Bio-oils Produced by Fast Pyrolysis of Two Energy Crops, *Energy and Fuels,* 22, 2104–2109

M. Mesa; Caio G. Sánchez; Elisabete M. S. Sanchez; Juan M. M. Pérez; Nakédia M. F. Carvalho (2013). Physicochemical Properties of Pyrolysis Bio-Oil from Sugarcane Straw and Sugarcane in Natura. *Journal of Biomaterials and Nanobiotechnology, 4*, 10-19. doi: 10.4236/jbnb.2013.42A002

Nigam, P. S., and Singh, A. (2011). Production of liquid biofuels from renewable resources. *Progress in Energy and Combustion Science, 37*(1), 52-68. doi: 10.1016/j.pecs.2010.01.003

Ozbay, N., Pütün, A., and Pütün, E. . (2006). Bio-oil Production from Rapid Pyrolysis of Cottonseed Cake: Product Yields and Compositions. *International Journal of Energy Research, 30*(7), 501-510.

Park, H., Heo, H., Park, Y., Yim, J., Jeon, J., Park, J., Ryu, C., and Kim, S. (2010). Clean Bio-Oil Production from Fast Pyrolysis of Sewage Sludge: Effects of Reaction Conditions and Metal Oxide Catalysts. *Bioresource Technology, 101*, S83-S85.

Salehi, E., Abedi, J., and Harding, T. . (2011). Bio-Oil from Sawdust: Effect of Operating Parameters on the Yield and Quality of Pyrolysis Products. *Energy and Fuels, 25*(9), 4145-4154.

Savage, P. D. a. P. E. (2011). Hydrothermal Liquefaction of a Microalga with Heterogeneous Catalysts. *Ind. Eng. Chem. Res.*(50), 52-61.

Sawant, S., Baravkar, A.,Kale, R. . (2011). FT-IR Spectroscopy Princilple, Technique and Mathematics. *International Journal of Pharma and Bio Sciences, 2*(1).

Sidel J., and Haddok, J. (2012). Soy Fatty Acids as Sustainable Modifier for Asphalt Binders. Alternative Binders for Sustainable Asphalt Pavements. *Transportation Research E-Circular*(E-C165), 15-22.

Speight, J. G. (2014). *The Chemistry and Technology of Petroleum,* Boca Raton, FL: CRC Press.

Vardon, D. R., Sharma, B. K., Scott, J., Yu, G., Wang, Z., Schideman, L., Strathmann, T. J. (2011). Chemical properties of biocrude oil from the hydrothermal liquefaction of Spirulina algae, swine manure, and digested anaerobic sludge. *Bioresour Technol, 102*(17), 8295-8303. doi: 10.1016/j.biortech.2011.06.041

Wierzbicka, A., Lillieblad, L., Pagels, J., Strand, M., Gudmundsson, A., Gharibi, A., Swietlicki, M., Sanati, M., Bohgard, M. (2005). Particle emissions from district heating units operating on three commonly used biofuels. *Atmospheric Environment, 39*(1), 139-150. doi: 10.1016/j.atmosenv.2004.09.027

Zhou, D., Zhang, L., Zhang, S., Fu, H., and Chen, J. (2010). Hydrothermal Liquefaction of Macroalgae Enteromorpha prolifera to Bio-oil. *Energy and Fuels, 24*(7), 4054-4061. doi: 10.1021/ef100151h