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Molecular Weight and Heating Value of Lignin Extracted using Deep Eutectic Solvent.

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MOLECULAR WEIGHT AND HEATING VALUE OF LIGNIN EXTRACTED WITH DEEP EUTECTIC SOLVENT

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ABSTRACT

The molecular weight of lignin helps us to determine how lignin can be applied accurately in industry. The molecular weight can predict the behavior of lignin, and how it will function when combined with other materials. This thesis discusses how the molecular weight of lignin can be found with gel permeation chromatography (GPC) after acetylation with acetic anhydride and pyridine. Different lignins gave different number average molecular weight and weight average molecular weight values, which were likely due to the biomass source, type of extraction and solubility in the solvent of choice. How the structure of lignin changed after derivatization was investigated using infrared spectroscopy. The extraction of lignin, including yields and purities, from various biomass sources using different deep eutectic solvents (DES) was also studied. Using bomb calorimetry, the fuel value of lignin extracted with DES from various biomass sources was also explored to determine the best method to obtain lignin-derived fuels.

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DEDICATION

I would like to thank almighty God for granting me the longevity of life to see this project completed. I would also like to thank my parents for their support financially all throughout out the duration of this project.

TABLE OF CONTENTS

ABSTRACT iii

APPROVAL FOR SCHOLARLY DISSEMINATION iv

DEDICATION v

LIST OF FIGURES viii

LIST OF TABLES x

ACKNOWLEDGMENTS xi

CHAPTER 1 INTRODUCTION 1

1.1 Background 1

1.2 Polymer Structure of Lignin 2

1.3 Importance of the Molecular Weight of Lignin. 4

1.4 Lignin Characterization Using Gel Permeation Chromatography (GPC). 4

1.5 Multi Angle Light Scattering (MALS) as a Detector for the GPC. 5

1.6 Bomb Calorimeter ..... **Error! Bookmark not defined.**

1.7 Fourier Transform Infrared Spectroscopy (FTIR) ..... **Error! Bookmark not defined.**

1.8 Deep Eutectic Solvent (DES) 7

1.9 Acetylation (Derivatization) of Lignin 8

CHAPTER 2 MATERIAL AND METHODS 9

2.1 Material 9

2.2 Materials and Equipment. 10

2.3 Preparation of Deep Eutectic Solvent (DES) 11

2.4 Pretreatment/Extraction of Biomass 12

2.5 Acetylation of Lignin using Acetic Anhydride and Pyridine 13

2.6 Gel Permeation Chromatography (GPC) 14

2.7 FTIR Analysis of Underivatized and Derivatized Lignin 14

2.8 Determination of Higher Heating Value of Lignin (HHV). 15

CHAPTER 3 RESULTS AND DICUSSION 16

3.1 Mass yield of DES-Extracted Lignin and Recovered Biomass 16

3.2 Molecular Weight Distribution of DES Extracted Lignin from different Biomass Sources 20

3.3 FTIR Spectra for Underivatized and Derivatized DES-Extracted Lignin 22

3.4 Lignin to Cellulose Peak Area 27

3.5 Lignin Energy Value. 29

CHAPTER 4 CONCLUSIONS AND FUTURE WORK 31

4.1 Conclusion 31

4.2 Future Work 32

BIBLIOGRAPHY 33

LIST OF FIGURES

Figure 1-1: Common Lignin Linkages (Patil et al., 2016)..... 3

Figure 1-2: Acetylation Mechanism of Acetic Acid/Sodium Metabisulfite. a) Phenolic group; b) Alcoholic group (Behin et al., 2016)..... 8

Figure 3-1: Mass Yield of DES-Extracted Lignin and Biomass from Rice Husks 17

Figure 3-2: Mass Yield of DES-Extracted Lignin and Biomass from Bagasse..... 18

Figure 3-3: Mass Yield of DES-Extracted Lignin and Biomass from Corn Stover 19

Figure 3-4: Mass Yield of DES-Extracted Lignin and Biomass from Coffee Chaff..... 20

Figure 3-5: Corn Stover Lignin and Cellulose Vibration for Underivatized and Derivatized (AACC). 22

Figure 3-6: Corn Stover Lignin and Cellulose Vibration for Underivatized and Derivatized (LACC)..... 23

Figure 3-7: Corn Stover Lignin and Cellulose Vibration for Underivatized and Derivatized (FACC). 23

Figure 3-8: Coffee Chaff Lignin and Cellulose Vibration for Underivatized and Derivatized (AACC). 24

Figure 3-9: Coffee Chaff Lignin and Cellulose Vibration for Underivatized and Derivatized (FACC). 24

Figure 3-10: Coffee Chaff Lignin and Cellulose Vibration for Underivatized and Derivatized (LACC)..... 25

Figure 3-11: Bagasse Lignin and Cellulose Vibration for Underivatized and Derivatized (AACC). 25

Figure 3-12: Rice Husk Lignin and Cellulose Vibration for Underivatized and Derivatized (AACC). 26

Figure 3-13: Corn Stover Lignin to Cellulose Peak Ratio for Raw and Derivatized Lignin. 27

Figure 3-14: Coffee Chaff Lignin to Cellulose Peak Ratio for Raw and Derivatized Lignin. 28

Figure 3-15: Rice Husks Lignin to Cellulose Peak Ratio for Raw and Derivatized Lignin. 28

Figure 3-16: Bagasse Lignin to Cellulose Peak Ratio for Raw and Derivatized Lignin. 29

Figure 3-17: HHV Value for DES-Extracted Lignin from Different Biomass..... 30

LIST OF TABLES

Table 1-1: An Estimate of the Amount of Linkages found in Softwood and Hardwood Lignin 3

Table 1-2: FTIR Vibrations related to Lignin and Cellulose (Kumar et al., 2018) 7

Table 2-1: Ratio of Hydrogen Bond Donor and Acceptor in the Deep Eutectic Solvents. 12

Table 3-1: Mass Yield of DES-Extracted Lignin and Biomass from Rice Husks 17

Table 3-2: Mass Yield of DES-Extracted Lignin and Biomass from Bagasse 18

Table 3-3: Mass Yield of DES-Extracted Lignin and Biomass form Corn Stover 18

Table 3-4: Mass Yield of DES-Extracted Lignin and Biomass form Coffee Chaff 19

Table 3-5: Average Molecular Weight Values of DES-Extracted Lignin. 20

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CHAPTER 1

INTRODUCTION

1.1 Background

As an integral component of cell walls, lignin is the second most abundant component of plants after cellulose and hemicellulose. It is made of three cross linked monolignols namely, courmaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S) (Zakzeski et al., 2010). Every plant has different amounts of monolignols. Coniferyl alcohol is found almost exclusively in softwood. Amounts of G and S are similar in hardwood (Fengel and Wegener 1984). Paper mills produce large amounts of lignin waste that are a component of black liquor. Due to the structure of lignin as a polymer, in the last few years, its structure has been researched to find useful applications. It has been used as a partial substitute for asphalt binder (Arafat et al., 2019). In the oil and gas industry, it is also used as a partial replacement for petroleum-based aromatic chemicals and composites (Koike, 2012). Some examples include lignin-based polymers (Koike, 2012), lignin-based carbon fibers (Kadla et al., 2002), and lignin fiber composite materials (Thielemans et al., 2002). Lignin's complex structure is difficult to understand, hindering many scholarly researchers in finding useful applications. The partial solubility and rigidity of lignin in various solvents has proved to be a challenge in investigating the structure of lignin.

1.2 Polymer Structure of Lignin

Lignin as a polymer has many interunit linkages and functional groups present. The linkages most found are ***β***-O-4, 5-5, ***β***-1, and ***β***-***β*** as shown on Table 1 (Zakzeski et al., 2010). The number and type of lignin linkages differs depending on the biomass source and method of extraction. ***β***-O-4 had a higher occurrence among the linkages. Phenyl glycosidic, esters, and benzyl ethers bond linkages in lignin show covalent bonding with carbohydrates. This bond structure is known as lignin-carbohydrate complexes (LCC) (Lapierre et al., 1991). These LCCs make it challenging to separate the lignin from the biomass. Additionally, the presence of ester or ether bonds accompanied by covalent bonds between cellulose and lignin is also present in softwood biomass. The presence of ester and/or ether bonds has been confirmed (Bidlack et al., 1992). This was elucidated by comparing the natural abundance oxygen isotope ratio (18O/16O) of cellulose from different processing methods and noting that breaking the ester and ether bonds should result in exchange of oxygen between the processing medium and lignin/cellulose (Zhou et al., 2010). A large lignin/cellulose ratio indicates the presence of ester and ether bonds between lignin and cellulose. These bonds will also lead to a higher amount of ^{18}O (Zhou et al., 2010). Additionally, the type of bonding present and the cleavage between cellulose and lignin also determines the $^{18}O/^{16}O$ isotope ratio (Xu,1991: Zhou 2019).

The percentage of ***β***-O-4 linkages in lignin varies depending on the proportion of S, G, and H units. In the S unit, the aromatic ring has methoxy groups at the 3rd and 5th position that prevent the formation of ***β***-5. 5-5, or dibenzodioxocin linkages, consequently the ratio of S/G/H affects the amount of ***β***-O-4 linkage in lignin (Patil et al., 2016). Table 1-1 gives an estimate of the amount of lignin found in softwood and hardwood. Also, Figure 1-1 shows the common linkages in lignin and their structure.

Table 1-1: An Estimate of the Amount of Linkages found in Softwood and Hardwood Lignin

Linkages	Estimate of lignin (%)	
	Hardwood	Softwood
β-O-4	60	45-50
5-5	5	18-25
β-5	6	9-12
4-O-5	7	4-8
β-1	7	7-10
β-β	3	3

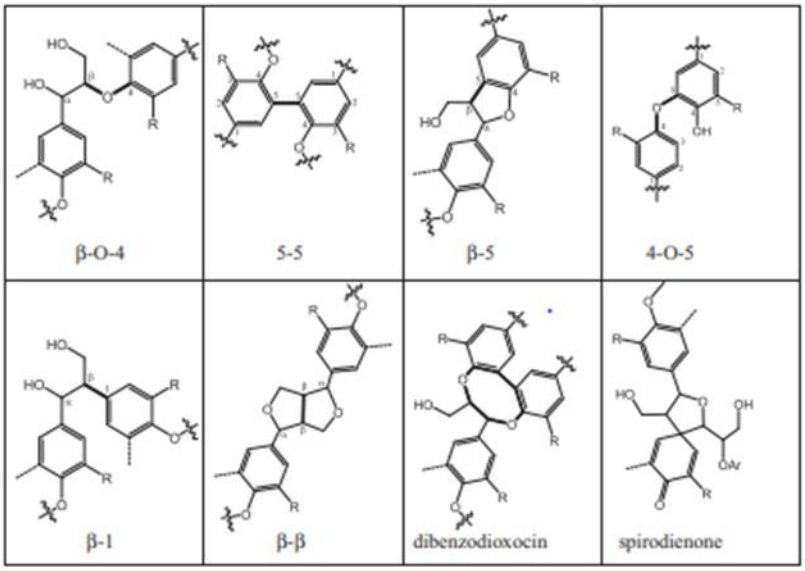

Figure 1-1: Common Lignin Linkages (Patil et al., 2016).

1.3 Importance of the Molecular Weight of Lignin.

Lignin has been extensively researched to determine the polymer structure and interlinkages to find alternative uses. The molecular weight of lignin gives some information about the stoichiometry or change happening when lignin is processed and how that affects the blending or composite properties of lignin. The combination of aromatic polymers resulting from 4-hydroxyphenylpropanoids linkages is what is known as lignin (Boerjan et al., 2003; Ralph et al., 2004). There are some underlying reasons why lignin molecular weight is important, some of which are:

1) Lignin, being the second most abundant biomass, is a key renewable resource that can reduce greenhouse gas emission.
2) The oxidative coupling of monolignols makes lignin an amorphous biopolymer.
3) The complex interunit linkages make lignin a difficult material to characterize and use in industry. Therefore, a foundational understanding of lignin is key to determining its value-added application.
4) The molecular weight distribution tells us about the reactivity and physicochemical properties of lignin.

GPC is a versatile tool that reveals the number average (Mn) and weight average molecular (Mw) weight of lignin. (Yoshida et al., 1993: Kubo et al., 1996: Jeong et al., 2013: Ponteau et al., 2003).

1.4 Lignin Characterization Using Gel Permeation Chromatography (GPC).

GPC is a form of size exclusion chromatography (SEC) that separates components or chemical species based on size (Lathe et al., 1956). The separation of the components takes place in a column with a pore size distribution close to the hydrodynamic volume of the sample being

analyzed (Paul-Dauphin et al., 2007). Since the molecules are separated by their size, small molecules will travel through different pores and take a long time to come out of the column, while large molecules, because of their size, travel a lot faster since they cannot penetrate most of the pores (Paul-Dauphin et al., 2007). When characterizing polymers, the dispersity (D) and molecular weight are critical factors to consider (Moore, 1964). The definitions for molecular weight include: number average molecular weight (Mn), weight average molecular weight (Mw), size average molecular weight (Mz), or the viscosity molecular weight (Mv) (Moore, 1964). The molecular weight at the highest peak can also be calculated and this is known as Mp. Unlike other separation techniques that depend on the physical and chemical interaction, GPC separates the particles based on the hydrodynamic volume of the chemical species or components being separated (Skoog 2006). For the calibration of a GPC, polystyrene standards with dispersity of less than 1.2 are frequently used for calibration (Sandler et al., 1998). However, since polystyrene is usually very linear, as a standard, it is mostly useful when comparing it to another linear polymer (Sandler et al., 1998).

1.5 Multi Angle Light Scattering (MALS) as a Detector for the GPC.

In GPC, a detector helps in keeping track of the concentration changes in the eluting solvent. The different types of detectors can be grouped in two different ways:

1. The concentration detectors: This helps to determine the sample concentration. They include the differential refractometer or the refractive index (RI) detectors, ultraviolet (UV) absorption detectors, infrared absorption (IR) detectors, and density detectors.
2. The molecular weight sensitive detectors: This include the low angle light scattering (LALS) and multi angle light scattering (MALS) (Trathnigg, 1995).

During characterization of copolymers two detectors are usually used (Sandler, 1998). The two detectors frequently used for composition analysis are the UV and RI detectors (Pasch, 2000).

1.6 Bomb Calorimeter

A bomb calorimeter is used to measure the heat of combustion of a reaction. It is a constant-volume type of calorimeter. Electrical energy is used to ignite the fuel. The fuel then burns. The calorie content is calculated by the change in the temperature of the surrounding water. The bomb calorimeter gives the heating value of deep eutectic extracted lignin from the different biomass sources.

1.7 Fourier Transform Infrared Spectroscopy (FTIR)

One other technique useful in lignin characterization is the FTIR. The FTIR is a device that obtains the infrared spectrum of emission or absorption from a sample, which could be a solid, liquid or gas. The FTIR spectrometer works at a high spectral resolution and helps to collect spectral data from a wide spectral range (Mendelsohn 2007). FTIR works by shining a beam that contains many frequencies of light on a sample and them reads how well the beam is subsequently absorbed by the sample. A second data point is created, and the beam is adjusted to contain frequencies of different modifications. After the process is repeated over a short time span, a computer then interprets the data by working backwards to interpret what the absorption is at each wavelength (Mendelsohn, 2007). Lignin to cellulose ratios were determined by adding the vibrational areas for each spectrum that related to lignin and divided by the vibrational areas related to cellulose as shown by Table 1-2.

Table 1-2: FTIR Vibrations related to Lignin and Cellulose (Kumar et al., 2018)

Wavenumber (cm^{-1})	Band Assignment
858	C-H out of plane positions 2,5,6 of lignin (guaiacyl) ring
896	C1−H deformation with a ring vibration contribution for amorphous cellulose
1060	C-O stretching vibration for cellulose and hemicellulose
1162	C-O-C vibration in cellulose
1425	Crystalline cellulose
1515	Lignin aromatic ring skeletal stretch
1600	Lignin C=O stretching conjugated to the aromatic ring, aromatic ring vibration
1718	C=O stretching in unconjugated ketone, carbonyl and ester groups related to lignin

896, 1060, 1162, and 1425 cm^{-1} are cellulose-related vibrations. 858, 1600, and 1718 cm^{-1} are lignin-related vibrations.

1.8 Deep Eutectic Solvent (DES)

Acetylation of lignin involves the addition of an acetyl group to lignin. Highly biodegradable, deep eutectic solvents (DES) are low cost, have low volatility and are non-flammable and nontoxic (Francisco et al., 2013). They are formed by two compounds that hydrogen bond with each other. The two components are the hydrogen-bond donor and the hydrogen-bond acceptor. The combination of the two components leads to the production of a new compound that has a lower melting point than the initial individual components. DES are easy to prepare and have attracted a lot of attention in many fields. The intermolecular hydrogen bonds in DES transfer to break the strong hydrogen bonds between biomass components, making biomass highly soluble through DES pretreatment. These biomass components include lignin, cellulose and hemicellulose.

1.9 Acetylation (Derivatization) of Lignin

Acetylation of lignin involves the addition of an acetyl group to lignin. The acetyl group is made up of a carbonyl group double bonded to oxygen with a methyl group (CH_3). In the acetylation of lignin with acetic anhydride and pyridine, the primary alcohol and the phenolic hydroxyl group are acetylated. Figure 1-3 shows an acetylation mechanism.

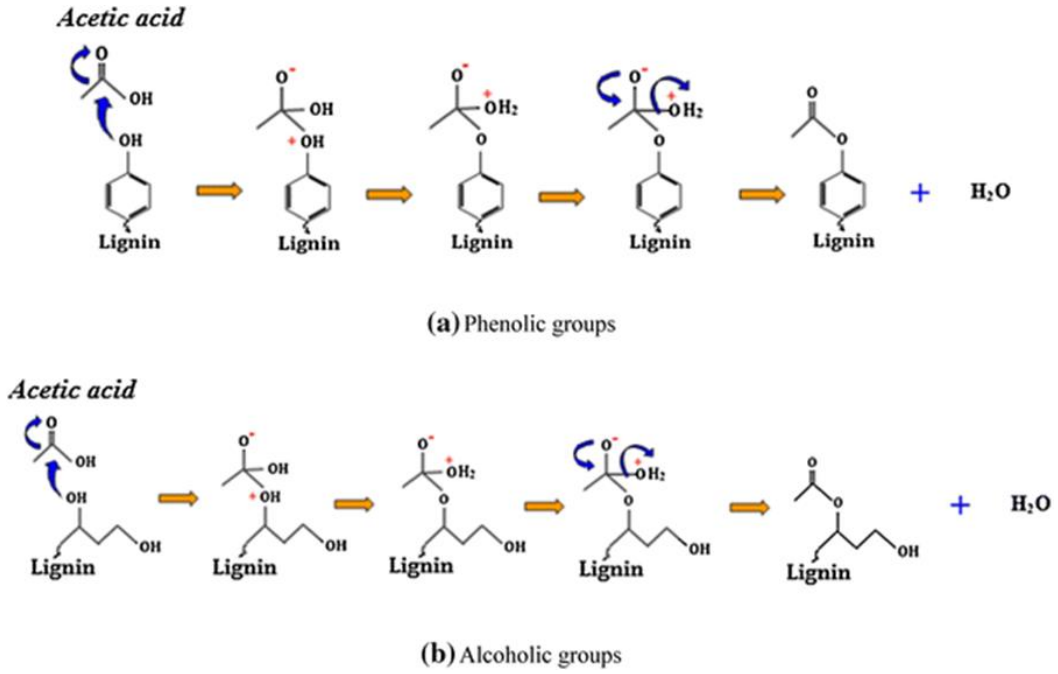

Figure 1-2: Acetylation Mechanism of Acetic Acid/Sodium Metabisulfite. a) Phenolic group; b) Alcoholic group (Behin et al., 2016).

CHAPTER 2

MATERIAL AND METHODS

2.1 Material

Lignin is the second most abundant component of plants after cellulose. Lignin accounts for approximately 20% of biomass. It is a very useful product economically, is generated in the production of paper, and can used a partial replacement of asphalt binder due to it being hydrophobic (Arafat et al., 2019). For the accurate and proper use of lignin, the molecular weight needs to the determined. Lignin molecular weight is not a straightforward calculation due to it being a complex polymer with many repeating units. The molecular weight of lignin gives an idea about the stoichiometry of the lignin reactions when it undergoes various physical and chemical changes. Currently, there is no gold standard for determining the molecular weight of lignin as different laboratories have come up different values for repeating experiments (Olumoye et al., 2018). The determination of the molecular weight of lignin has been a challenge because of its complex chemical structure and the polar and non-polar association reactions occurring between lignin and some known solvents. This interaction induces solute-solute, solute-solvent and solute-column interaction when the lignin undergoes GPC analysis (Asikkala et al., 2012). Additionally, lignin is insoluble in most solvents and this creates a problem when dissolving lignin in a solvent for analysis with GPC. To determine the molecular weight of lignin, GPC is used. However, lignin in its raw form cannot be analyzed to determine a close enough value for its correct molecular

weight. This is due to solubility issues in the solvent of choice, which in this case is tetrahydrofuran (THF). If lignin is not suitably soluble in THF, there will be solute-solute, solute-solvent and solute-column interactions. Derivatization using acetic anhydride and pyridine was chosen in this study to make the lignin soluble. It should be noted that even after derivatization the solubility of lignin in THF could still be partial. To solve this challenge of lignin insolubility in a solvent of choice, the lignin samples were derivatized by first acetylating them with acetic anhydride and pyridine. They were then subsequently dissolved in chloroform and diethyl ether. The solid part of these mixtures was subsequently dissolved in THF and taken for GPC analysis to determine their molecular weights. FTIR spectra were also run to determine the wavenumbers and different lignin to cellulose peak area ratios. The energy value of lignin samples were also determined using the bomb calorimeter.

2.2 Materials and Equipment.

There were four types of biomass evaluated in this study. The first was rice husks and these rice husks were obtained from Falcon Rice Mill in Crowley, Louisiana. Second, sugarcane bagasse was obtained from Lula Westfield, Inc. in Paincourtville, Louisiana. Corn stover was obtained from Idaho National Lab (Idaho Falls, ID). The coffee chaff came from Orleans Coffee in Kenner, Louisiana. Also, black liquor, from which black liquor lignin was extracted, was obtained from Graphic Packaging in Monroe, LA. The acetic acid, formic acid, lactic acid, and choline chloride used to produce the DES (involved in pretreating the biomass to break the multicomponent matrix) and ethanol were purchased from Millipore Sigma (Burlington, Massachusetts). Tetrahydrofuran (THF), the solvent the lignins were dissolved in before taking them for GPC analysis, was also from Millipore Sigma. Nylon filters and net filters used to filter the DES and biomass mixtures after pretreatment were obtained from GE Healthcare (Chicago, Illinois). Acetic anhydride and

pyridine used for derivatizing the lignins were obtained from Aqua Solutions Inc. (Deer Park, TX). A standard testing sieve (ASTM E-11 Specifications NO. 80) with 0.0070 inches, metric 180 μm mesh spacing from Thomas Scientific (Swedesboro, NJ) was used to sieve the biomass into uniform sizes. The vacuum pump used to speed up filtration was obtained from Gardner Denver Thomas Inc. (Milwaukee, WI). The oven used for drying lignin samples after extraction was obtained from Blue M Electric Co. (Blue Island, IL). Magnetic stirrers for stirring the mixture of acetic anhydride, pyridine and lignin were obtained from Troemner, Inc. (Thorofare, NJ). The rotary evaporator was obtained from Kori Instruments (Zhengzhou City, Henan Province, China). The centrifuge used for separation of solid derivatized lignin from a mixture of diethyl ether, chloroform and THF was obtained from International Equipment Corporation (Needham Heights, MA). The vacuum oven used for drying the derivatized lignin was obtained from Across International (Livingston, NJ). Additionally, the lignin samples were analyzed using a Mattson Genesis II Fourier Transform Infrared Spectroscopy (FTIR) from Mattson Technology (Fremont, CA, USA) using KBr pellets prepared containing the samples. For each sample, 32 scans were performed from 4000 to 400 cm^{-1} to determine the lignin and cellulose vibrations. Additionally, a 1341EB bomb calorimeter from Parr Instrument Co. (Moline,IL) was used to determine the energy value of the lignin extracted from the biomass.

2.3 Preparation of Deep Eutectic Solvent (DES)

The mole ratio of each hydrogen bond donor and hydrogen bond acceptor is shown in Table 2-1. These mixtures of these ratios were vortexed in a capped 50 ml vial. The mixture was subsequently put in an orbital shaker and left to shake at a temperature of 60 $^{\circ}C$ and a rotation speed of 200 RPM for 20 min. After forming a clear solution, all DES were then stored at room temperature. The mixtures remained clear solutions throughout the experimental period, as

expected. This resulted in a deep eutectic solvent that will deconstruct the biomass (Lynam et al., 2017).

Table 2-1: Ratio of Hydrogen Bond Donor and Acceptor in the Deep Eutectic Solvents.

Hydrogen bond donor.	Hydrogen bond acceptor	Mole ratio
Formic Acid	Choline Chloride	2:1
Lactic Acid	Choline Chloride	10:1
Acetic Acid	Choline Chloride	2:1

2.4 Pretreatment/Extraction of Biomass

Each selected biomass (coffee chaff, corn stover, rice husks, and bagasse) was sieved to the appropriate size of 180 μm or smaller. An oil bath was set to the appropriate temperature of 155 °C. We then measured out the selected biomass by weight (3 g) and put it in a clean, numbered vial (recording the mass). Subsequently DES was measured out by weight (30 g) and put it in the same vial (recording the mass). The vial with the DES, biomass, and a stir bead were then weighed and recorded. The vial was set into an oil bath, a rubber stopper is inserted, and the condenser lowered into it. The condenser drain hose was double checked to make sure it was in the drain. The water system was subsequently turned on and the system was left for two h. Two large (.44 micrometer) nylon filters, one net (mesh) filter, and one small nylon filter were dried for 30 min at 105 °C while the biomass was in the DES. One tin was designated for the biomass and another tin for the lignin that precipitated out of the solution. The tins were labeled with the experiment components (DE type, Biomass type, time, temperature), the date, and the type of material to be stored in it. A clean and dry vacuum flask was attached to a vacuum pump. A clean and dry funnel with a net filter was then inserted and the pump was turned on (making sure the hose joint was

slightly open) and the DES/biomass slurry poured into the filter slowly. The flask was then rinsed with approximately 5 mL of EtOH and poured into the funnel with the biomass. The vacuum pump was turned off and the biomass scraped back into the original flask, which was filled with 20 mL EtOH. A stir bead was added, and the flask was then placed on a magnetic stirrer for approximately 5 min. The vacuum filtration process was repeated with the same filter. The flask and the stir bead were rinsed with EtOH. The biomass was scraped back into the jar and a stir bead with approximately 75 ml of DI water was added. We then placed the jar with a closed lid into a water bath for 15 min at 50 °C. It was subsequently removed from the water bath, and the water decanted. Water was added and the process was repeated twice. After decanting 3 times, it was left soaking overnight. The funnel was then rinsed with ethanol into the vacuum flask, a stir bead was placed inside and this was left on a magnetic stirrer for 20 min. A large nylon filter (0.44 μm) was dried and placed in a large funnel. The vacuum pump was turned on and a good seal was ensured before pouring in the slurry. The mixture was poured into the funnel slowly to ensure the solids did not leak out. Then 175 ml of DI water was added to the large flask, leading to lignin precipitating out of the filtrate. The mixture was stirred on a magnetic stirrer for 20 min. During this time period the filter from the initial filtration step was placed in a labeled tin and left to dry for 24 h. A new filter was dried and weighed and used to filter out the DI precipitate (Lignin) after it was taken from the magnetic stirrer. It was then placed in a pre-labeled tin and left to dry for 24 h before weighing.

2.5 Acetylation of Lignin using Acetic Anhydride and Pyridine

A small flask was dried for 30 min and weighed. It was subsequently left in a desiccator to cool. A weighing paper was then used to weigh out a small amount of lignin (~ 0.05 g). The weighed lignin was then placed in a small flask. Volumes of 3 ml of acetic anhydride and 3 ml

pyridine were then added into the flask in a 1:1 ratio. A stir bead was then placed inside the flask to ensure proper mixing and the sample was left to react properly for 24 h. After proper mixing for 24 h., the sample was taken to the rotary evaporator and 600 ml of ethanol in 50 ml increments was added to each sample batch to remove the acetic anhydride and pyridine in the mixture. The sample was taken to the hood after which 2 ml of chloroform and 50 ml of diethyl ether were added to the sample. The mixture was centrifuged to ensure proper separation of the solid. After centrifuging, the sample was decanted, and a little liquid was left in the flask to aid the removal of solids. The remaining solid part mixed with the liquid was poured into a small flask and then taken to a vacuum oven and left to dry for 24 h at 40 °C and 2070 kPa. After drying the flask was then placed in a desiccator to cool down before weighing. The weight of the flask was subtracted from the initial weight of the flask. This subtraction gave the weight of dried lignin.

Dried lignin was dissolved in THF to a set concentration, usually 3-5 mg/ml. The mixture was left to dissolve in the THF for 2 weeks. After 2 weeks it was filtered into a paraffin vial through a 0.4 µm syringe filter. The sample was then taken for analysis with GPC.

2.6 Gel Permeation Chromatography (GPC)

The sample was analyzed on a GPC machine using polystyrene as a standard. The GPC unit was produced by Agilent technologies (Santa Clara, CA). The GPC columns were manufactured by Phenomenex (Torrance, CA). The samples were analyzed using ASTRA software.

2.7 FTIR Analysis of Underivatized and Derivatized Lignin

FTIR samples were prepared using potassium bromide (KBr) pellets. A background of a 100 mg KBr pellet was first prepared, after which 1 mg of biomass sample and 100 mg of KBr

were mixed. The mixture of KBr and sample was ground together, producing a uniform color. The mixture of sample and KBr was funneled inside an anvil. Another small anvil was placed on top with the shiny side down and a larger anvil was placed on it. They were then placed inside a pellet presser and pressed to produce a compact pellet with the KBr portion looking clear.

The pellet was then placed in a holder (two thin magnets with a pellet-sized hole in the middle). The FTIR device was turned on and the OMNIC program used for analyses of the spectra was also opened. The experimental setup of the software was set to 32 scans and 2 cm^{-1} resolution.

The door of the machine was then opened and the holder containing the pellet of sample and KBr was slid in. When the scans were complete, spectra were saved.

2.8 Determination of Higher Heating Value of Lignin (HHV).

A fuse wire was initially weighed and recorded (~10 cm), A sample of about 0.4 g to 0.5 g was then placed in a pre-weighed crucible. The weight of the crucible and the fuse wire were then recorded. The sample and crimp fuse wire were subsequently placed in the sample holder to ensure the fuse wire just touched the sample. The sample holder was then placed in a bottom vessel and a screw cap was screwed to ensure proper sealing. The valve on the top was closed. An oxygen hose from an oxygen cylinder was then attached to the top and a valve was turned slowly to get to 25 atm pressure inside the vessel. The oxygen hose was removed, and the vessel was placed in a dewar. Electrodes were plugged in, and 1 liter of water was added to the dewar. A rubber gasket placed on a horizontal wheel at the top of the dewar permitted stirring of the water.

The ignition was turned on and when the temperature stabilized, it was recorded. The stirrer was then then turned off, the gasket and thermometer removed, and the vessel was carried to the hood. The top value was slowly unscrewed to release the pressure. The crucible and fuse wire were then reweighed.

CHAPTER 3

RESULTS AND DICUSSION

3.1 Mass yield of DES- Lignin and Recovered Biomass Extracted

The lignins from all the sources of biomass were extracted and the lignin yield from each correlated to the documented amount of lignin present in each biomass; 12% for bagasse, 17% for rice husks, 17% for corn stover and 23% in coffee chaff (Ballesteros et al., 2014). The ratio of lignin % to mass yield % recovered, gives us the percentage of lignin extracted from each sample. We then found the ratio of this value to the known approximate value of lignin present in the biomass according to literature, as initially stated. This gave us an approximation of the purity of each lignin extracted. Lignin of 100% purity is hard to achieve because of variability in the extraction process. Hence, the molecular weight values of these lignins was expected to be imperfect because these impurities show up on chromatograms when the derivatized samples are analyzed on the GPC. LA:CC seemed to have the highest purity for lignin recovered for most of the biomass types. This might be due to the higher ratio of lactic acid to choline chloride used to prepare the DES (10 to 1 moles of lactic acid to choline chloride). AA:CC appeared to be the second best in purity. FA:CC pretreatment. gave the lowest purity. It should be noted this definition for purity of the lignin samples is qualitative. Table 3.1, 3.2, 3.3, 3.4, shows the purity, lignin percent and mass yield of DES extracted lignin from rice husks, bagasse, coffee chaff, and corn stover respectively. Figure 3-1, 3-2, 3-3, 3-4, compares the mass yield and purity of lignin extracted with different DES from a specific biomass source.

Table 3-1: Mass Yield of DES-Extracted Lignin and Biomass from Rice Husks

	FA:CC	LA:CC	AA:CC
Mass Yield %	64.13	65.00	75.76
Lignin %	19.95	13.23	19.04
Purity %	61.08	93.33	75.10

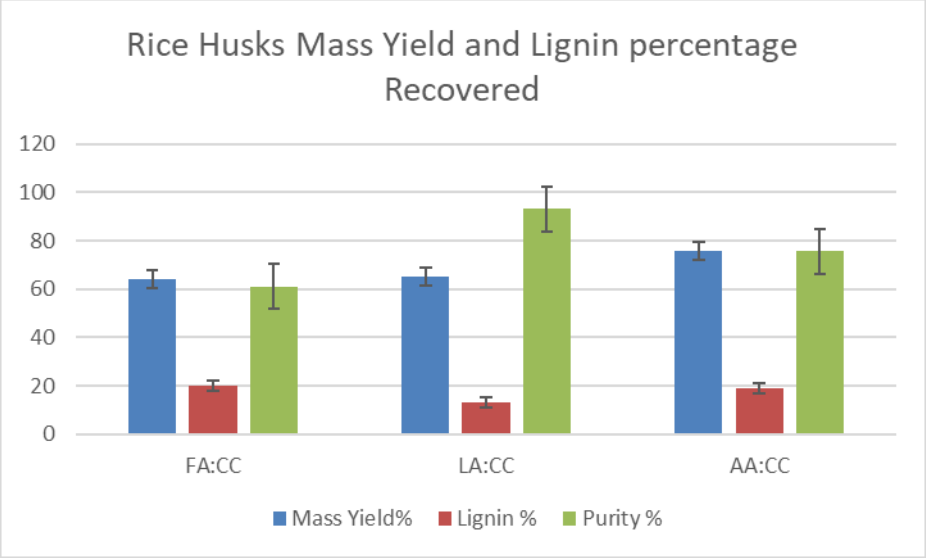

Figure 3-1: Mass Yield of DES-Extracted Lignin and Biomass from Rice Husks.

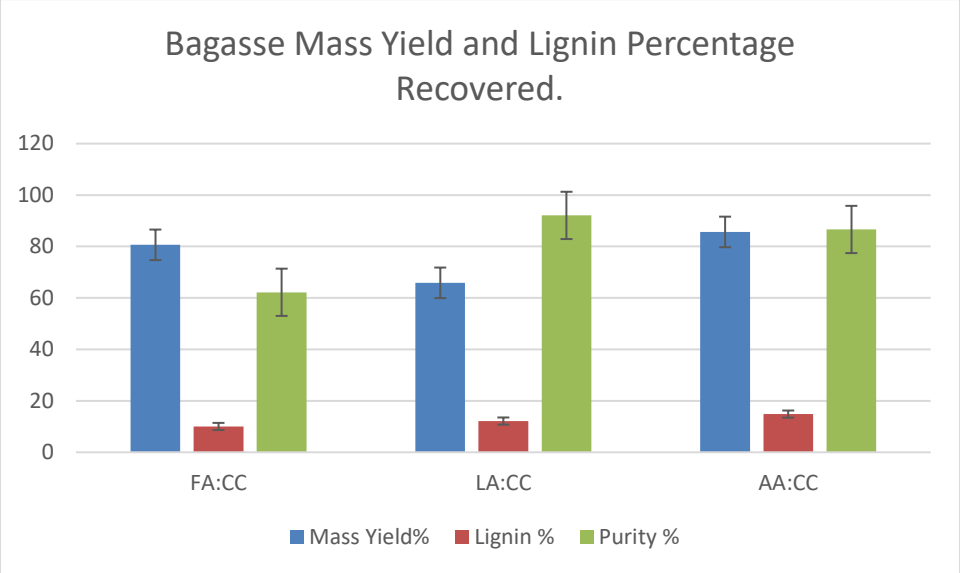

Figure 3-2: Mass Yield of DES-Extracted Lignin and Biomass form Bagasse

Table 3-2: Mass Yield of DES-Extracted Lignin and Biomass from Bagasse.

	FA:CC	LA:CC	AA:CC
Mass Yield %	80.65	65.87	85.66
Lignin %	10.03	12.13	14.84
Purity %	62.20	92.09	86.62

Table 3-3: Mass Yield of DES-Extracted Lignin and Biomass form Corn Stover

	FA:CC	LA:CC	AA:CC
Mass Yield%	62.63	68.34	66.18
Lignin %	11.09	13.12	10.63
Purity %	84.32	91.43	76.47

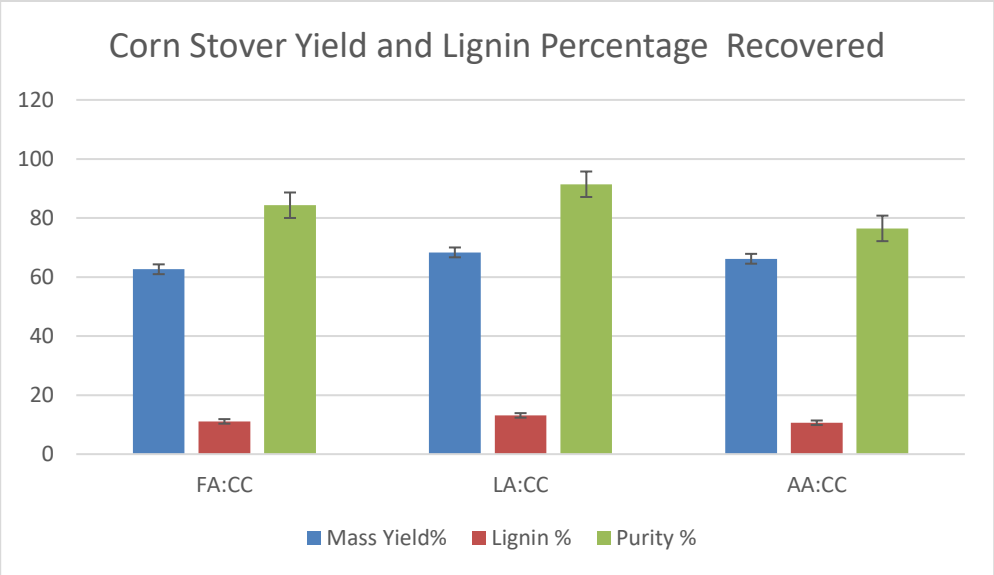

Figure 3-3: Mass Yield of DES-Extracted Lignin and Biomass from Corn Stover.

Table 3-4: Mass Yield of DES-Extracted Lignin and Biomass from Coffee Chaff.

	AACC	FACC	LACC
Mascs Yield %	65.97	69.46	76.36
Lignin Yield %	14.80	12.28	9.63
Purity %	94.64	74.59	53.24

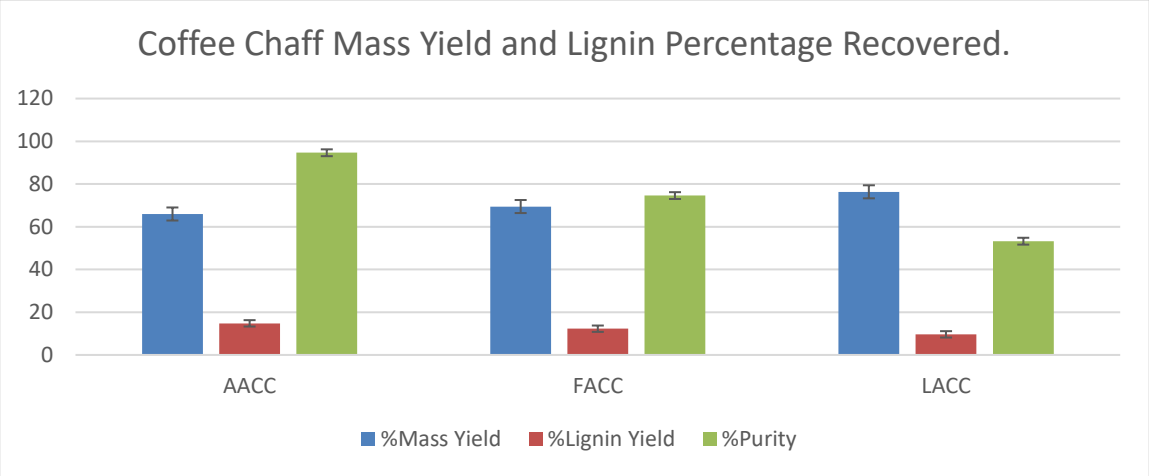

Figure 3-4: Mass Yield of DES-Extracted Lignin and Biomass from Coffee Chaff

3.2 Molecular Weight Distribution of DES Extracted Lignin from different Biomass Sources

The molecular weight values on Table 3-5 shows that the weight average molecular weight (Mw) of the different biomass samples was higher than the number average molecular weight (Mn) and the molecular weight of the highest peak (Mp).

Table 3-5: Average Molecular Weight Values of DES-Extracted Lignin

Average of Molecular Weight Values					
	DES	Mn(KDa)	Mw(kDa)	Mp(KDa)	PDI
Rice husk	FA:CC	270.60	323.10	145.73	1.20
	LA:CC	134.13	174.50	67.40	1.31
	AA:CC	77.50	115.03	53.90	1.89
Bagasse	FA:CC	130.70	181.70	67.60	1.39
	LA:CC	150.23	204.23	71.53	1.39
	AA:CC	33.58	77.23	26.79	1.92
Coffee-Chaff	FA:CC	262.35	297.65	176.85	1.14
	LA:CC	58.08	97.20	28.75	1.74
	AA:CC	466.55	495.55	324.00	1.06
Corn stover	FA:CC	76.80	93.60	52.80	1.47
	LA:CC	243.05	291.50	163.46	1.23
	AA:CC	242.78	302.02	153.85	1.26
Black liquor Lignin	Sulphuric Acid	300.85	316.15	275.75	1.05

The molecular weight values are also analogous to the known values of softwood lignin. (Tolbert et al., 2014). The polydispersity value (PDI) indicated a relatively broad range of molecular weight. A wide molecular weight distribution tends to lead to reduced viscosity when these lignins are added to substances (Saba et al., 2018). Thus, bagasse and rice husks pretreated with AACC, which show a high PDI, would be expected to act as plasticizers when added to binders such as asphalt or cement.

The lowest molecular weight was found for AACC extracted lignin from bagasse, followed by coffee chaff lignin from LACC pretreatment. PDI tended to have an inverse relationship with Mw, suggesting that the more lignin bonds were broken, the greater the range of Mw. For lignin extracted from rice husks, AACC was the most effective in reducing molecular weight. FACC pretreatment gave the lowest molecular weight for corn stover lignin. If the black liquor lignin is considered as a control, each lignin could achieve a lower molecular weight when extracted with any DES, except for rice husks with FACC pretreatment. Although each of the biomass, since they are herbaceous, would be expected to have G, S, and H type lignin, the most effective DES varied for the biomass. This finding means that different DES may need to be investigated for a specific biomass to find the one most suited for that biomass' deconstruction.

The purity of our samples in THF can be said to be relative because for the analyses of the molecular weight using the GPC, the chromatograms showed peaks of different substances not necessarily associated with the lignin peaks. These impurities can be due to the extraction and processing of the biomass sample. Tables 3.2 and 3.3 show that the lignin is not 100% pure. Additionally, the question of solubility of the derivatized lignin in our solvent of choice (THF) also arises because of the long time the sample was left to dissolve in THF. Lignin derivatized using acetic anhydride and pyridine is only partially soluble in THF (Baumberger et al., 2007).

Another factor to consider is the refractive index increment (dn/dc). It should be noted that since a polystyrene standard was used in the determination of the molecular weight with the GPC, the dn/dc value was based on polystyrene. It has been reported that dn/dc changes after chemical modifications because the value of dn/dc for chitosans was found to be dependent on the acetylation and dissociation degree (Sorlier at al., 2003).

3.3 FTIR Spectra for Underivatized and Derivatized DES-Extracted Lignin

For the different lignins, the effect of derivatization with acetic anhydride and pyridine on the lignin and cellulose vibration areas was explored and wavenumbers are shown on Figure 3-5, 3-6, 3-7, 3-8, 3-9, 3-10, 3-11, and 3-12.

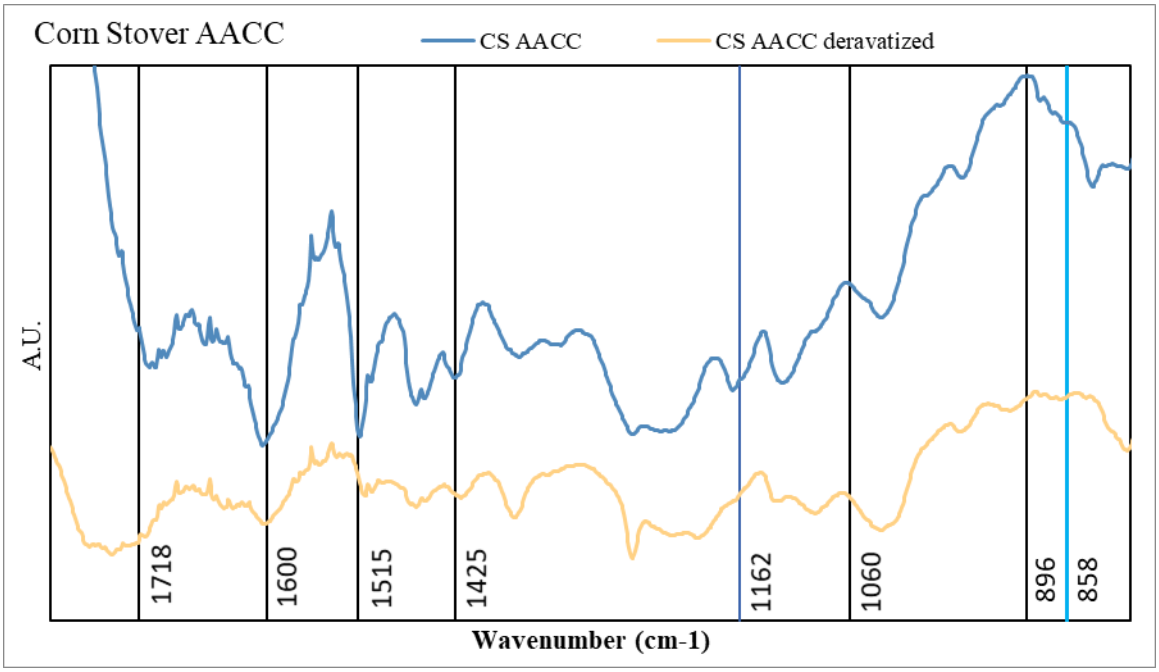

Figure 3-5: Corn Stover Lignin and Cellulose Vibration for Underivatized and Derivatized (AACC)

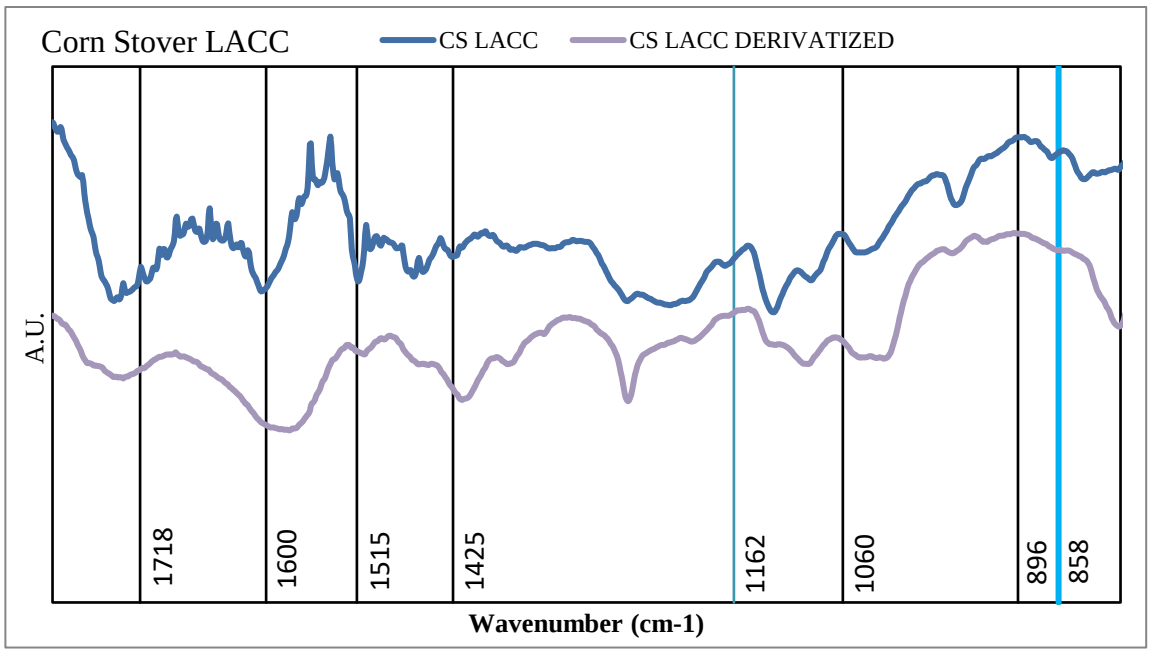

Figure 3-6: Corn Stover Lignin and Cellulose Vibration for Underivatized and Derivatized (LACC).

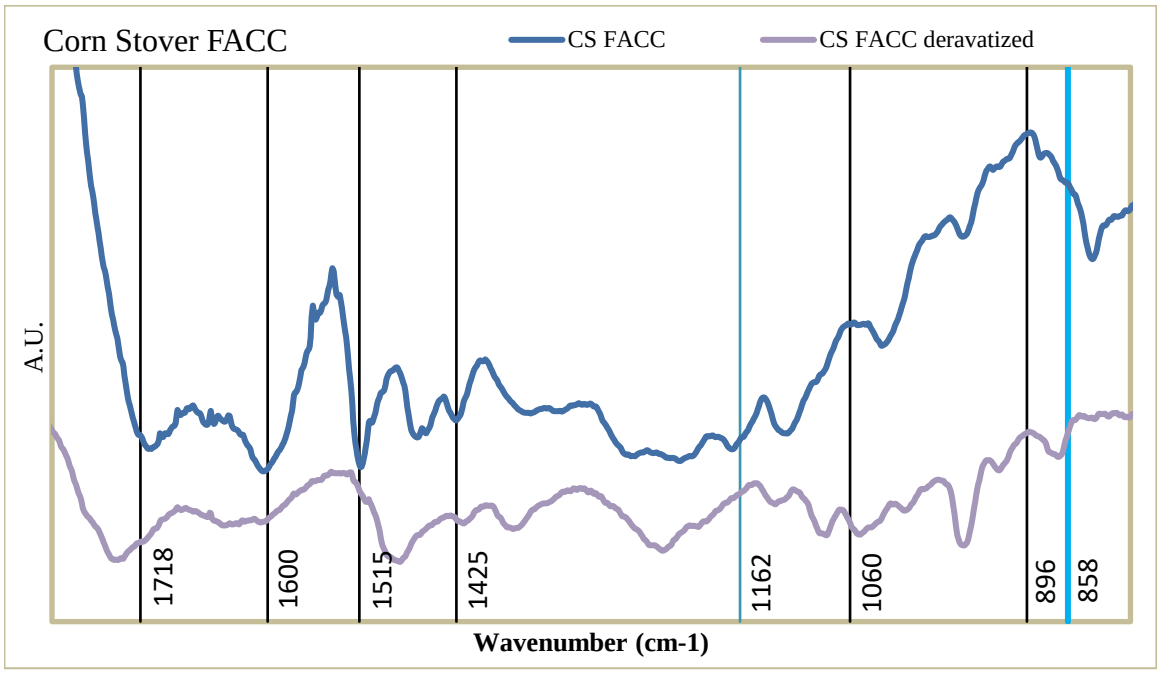

Figure 3-7: Corn Stover Lignin and Cellulose Vibration for Underivatized and Derivatized (FACC).

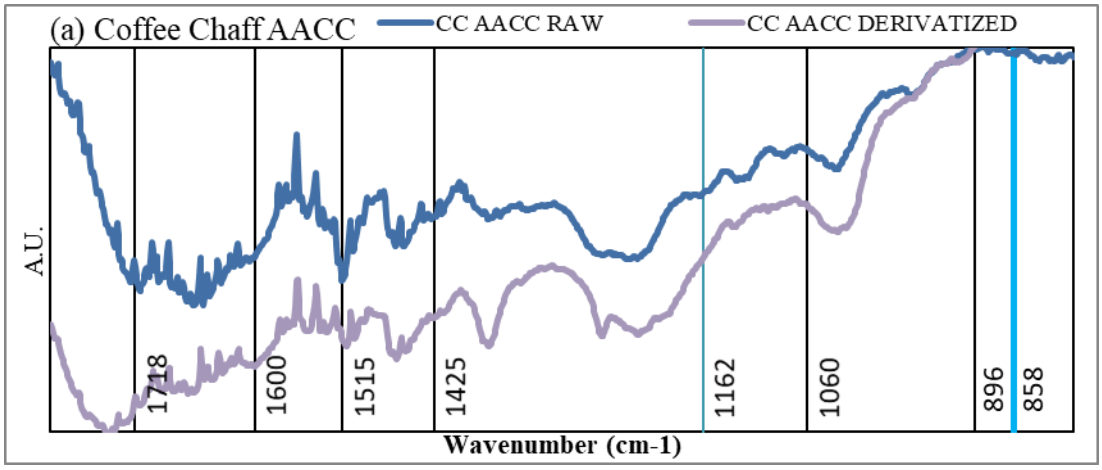

Figure 3-8: Coffee Chaff Lignin and Cellulose Vibration for Underivatized and Derivatized (AACC).

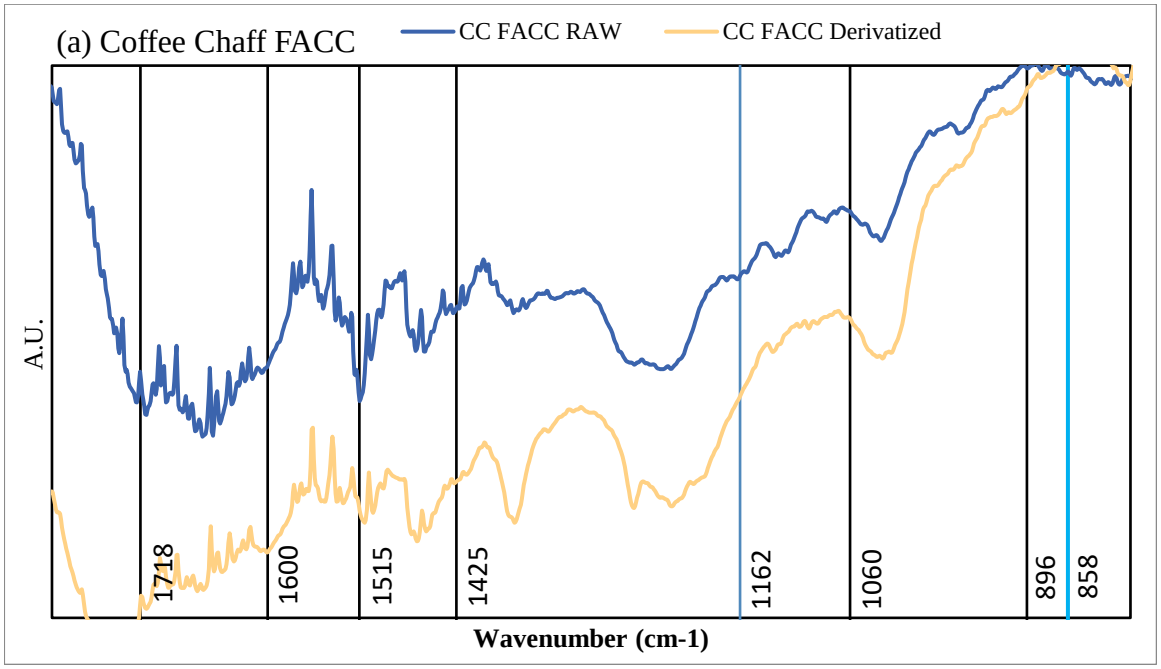

Figure 3-9: Coffee Chaff Lignin and Cellulose Vibration for Underivatized and Derivatized (FACC).

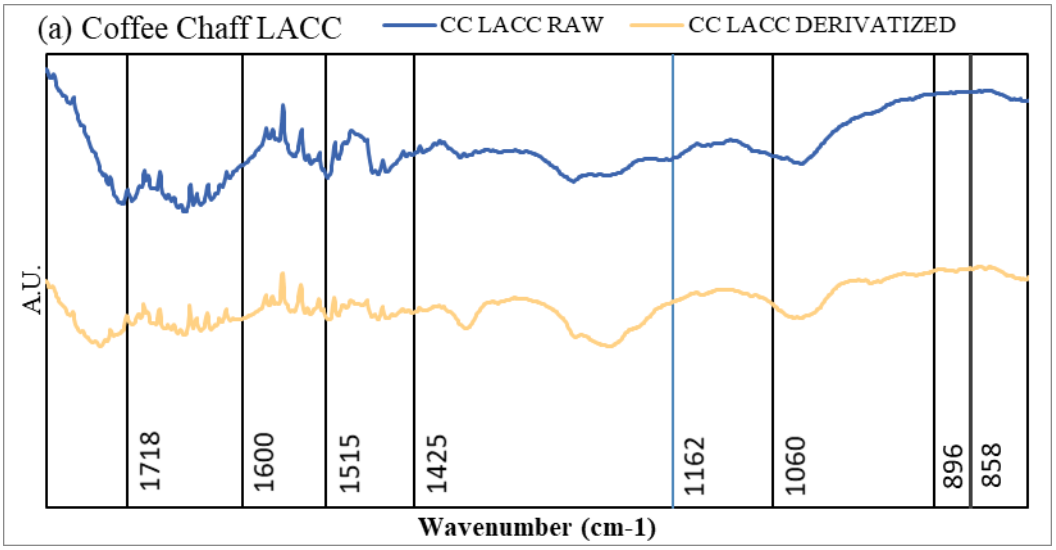

Figure 3-10: Coffee Chaff Lignin and Cellulose Vibration for Underivatized and Derivatized (AACC).

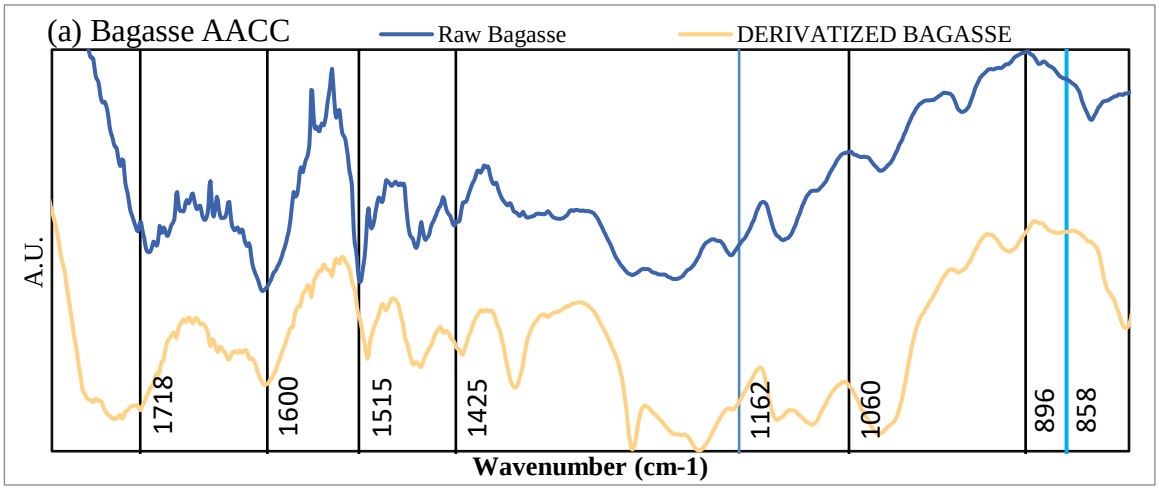

Figure 3-11: Bagasse Lignin and Cellulose Vibration for Underivatized and Derivatized (AACC).

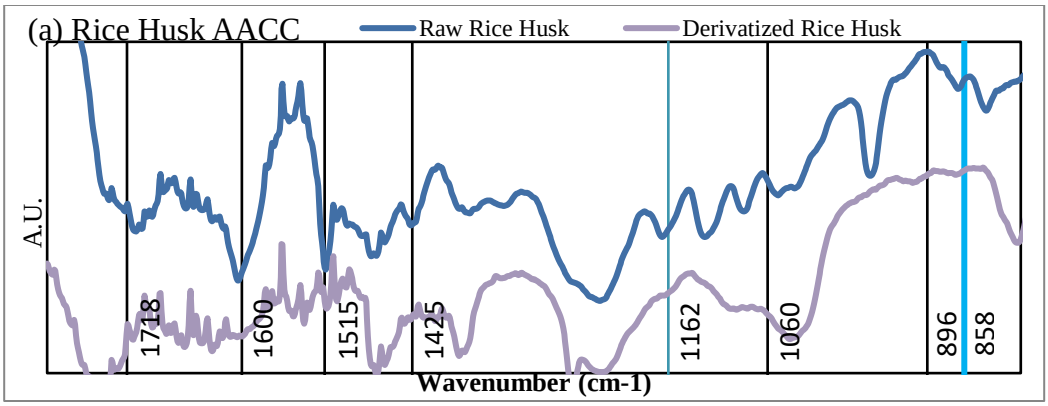

Figure 3-12: Rice Husks Lignin and Cellulose Vibration for Underivatized and Derivatized (AACC).

For all the FTIR spectra shown there is a change in the peak area for the underivatized and derivatized lignin. This is very noticeable especially in the C-H out of plane positions 2,5,6 of lignin (858 cm^{-1}) related wavenumber. This is due to the acetylation with acetic anhydride and pyridine because acetylation replaces the C-H bond with C=O (1718 cm^{-1}). A blue shift at 1718 cm^{-1}, a C=O lignin-related vibration is evident with derivatization in Figures 3-5 through 3-12. Acetylation helps to improve the solubility of lignin in THF and thus minimizes solute-solute, solute-solvent and solute-column interactions. These interactions typically affect the analysis of the samples in the GPC as they block the light scattering effect that is critical for the accurate determination of the molecular weight.

3.4 Lignin to Cellulose Peak Area

The variability in the extraction process can be said to affect the variability in the lignin to cellulose vibrational area ratio. The acetylation produces more C=O groups. Therefore, there should be more C=O stretching and consequently a larger peak area for this wavenumber (1718 cm^{-1}) after acetylation with acetic anhydride and pyridine. However, incomplete solubility and partial acetylation might affect the occurrence of C=O stretching. This also affects the peak area when the samples spectra are analyzed with FTIR. These inconsistencies in the lignin to cellulose ratio were observed for all the lignin samples analyzed with different deep eutectics (Figure 3-13).

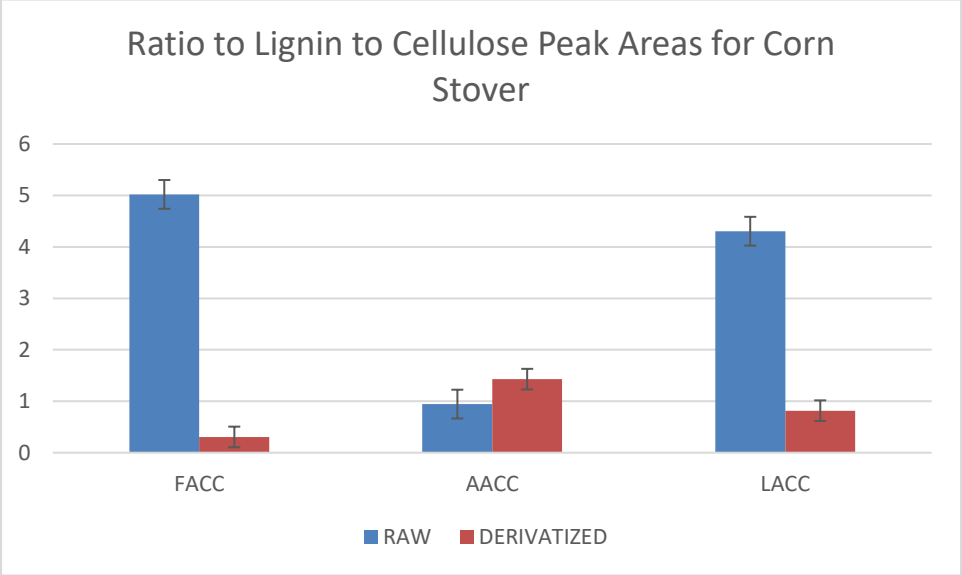

Figure 3-13: Corn Stover Lignin to Cellulose Peak Ratio for Raw and Derivatized Lignin.

From this deduction it can be inferred that the lignin to cellulose ratio can be an indicator of how well a sample is derivatized with acetic anhydride and pyridine. This inconsistency should be investigated further. Figure 3-14, 3-15, 3-16, also shows the inconsistencies for different lignins, when extracted with DES from the biomass sources investigated.

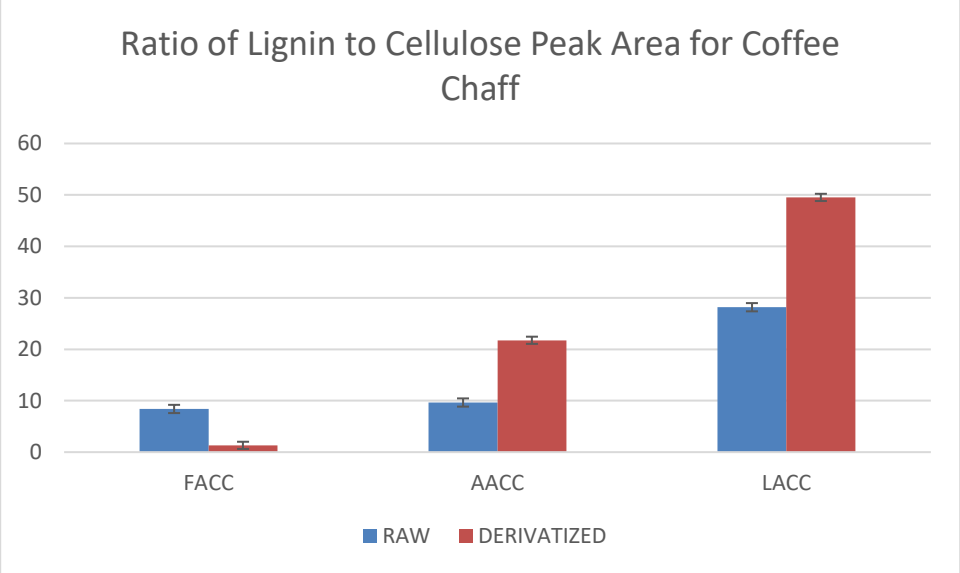

Figure 3-14: Coffee Chaff Lignin to Cellulose Peak Ratio for Raw and Derivatized Lignin

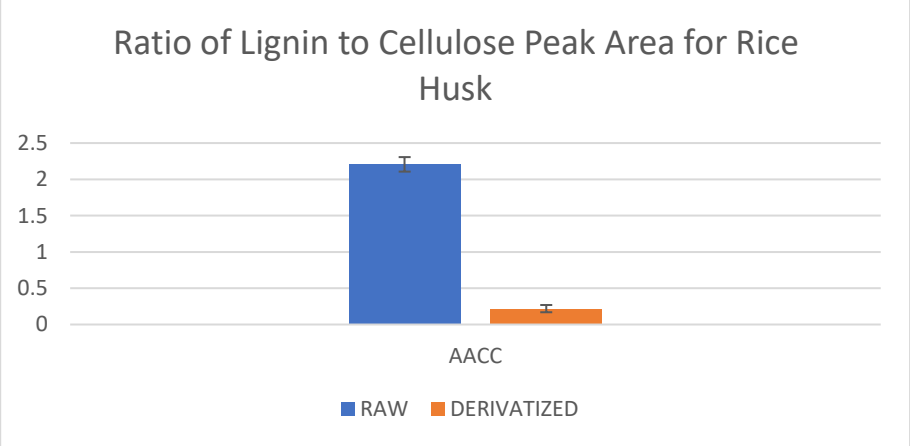

Figure 3-15: Rice Husks Lignin to Cellulose Peak Ratio for Raw and Derivatized Lignin

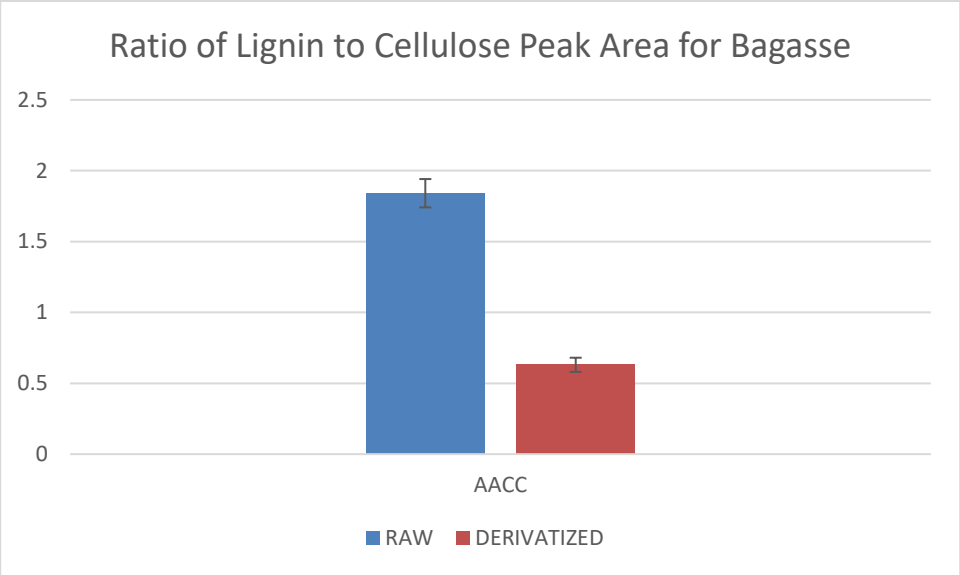

Figure 3-16: Bagasse Lignin to Cellulose Peak Ratio for Raw and Derivatized Lignin

3.5 Lignin Energy Value.

Figure 3-17 shows the higher heating value (HHV) of lignin from different biomass sources. Lignin from corn stover, bagasse and rice husks extracted with AACC showed the highest HHV and it is significantly higher than the HHV value from our reference black liquor and alkaline lignins. Coffee chaff lignin extracted with AACC gave us the smallest HHV and is the only biomass source that has a lower energy value than the controls black liquor and alkaline lignins. The oxygen pressure used might have reduced the heating value of these biomass because these samples were run at an oxygen pressure of 25 atm, but the recommended oxygen pressure is 30 atm (Shen et al., 2012). The samples had an average mass of 0.43±0.01 g so the mass of each sample analyzed were analogous. All the samples were herbaceous, and so were likely a mixture of H, S, and G lignins, but the alkaline control was likely derived from softwood, which has primarily G lignin. The percentage of unburned material is subtracted from the mass that the HHV is calculated with, so large variation in the number of inorganics can affect the HHV found.

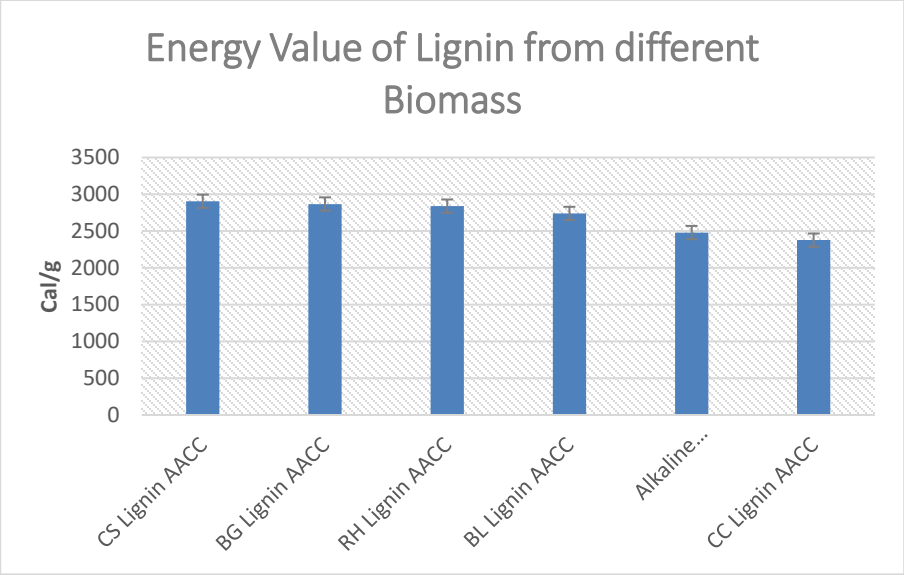

Figure 3-17: HHV Value for DES-Extracted Lignin from Different Biomass.

CHAPTER 4

CONCLUSION AND FUTURE WORK

4.1 Conclusion

Biomass from different sources have different types and lignin percentages in them. The structure, pretreatment and extraction method determine how they can be analyzed and applied effectively in the industry. The purity (carbohydrate content, ash, metals, sulfur, extractives and lignin content), molecular structure (molecular mass, molecular mass distribution, molecular size, functional groups) and thermal properties such as the heating value are some of the most important lignin characteristics, but there are still no uniform standardization method. (Xie et al., 2016). LACC pretreatment of biomass gave the best purity and AACC was more effective than the other DES in separating the lignin from the biomass. Corn stover lignin from AACC pretreatment gave the highest fuel value, while coffee chaff lignin from AACC pretreatment yielded the lowest fuel value. AACC extracted lignin had the lowest molecular weight for rice husk and bagasse. LACC pretreatment of coffee chaff gave the lowest molecular weight for this biomass. The lowest molecular weight for corn stover lignin was obtained with FACC pretreatment. Additionally, using black liquor lignin as control, each lignin could achieve a lower molecular weight when extracted with DES. A wide molecular weight distribution was obtained from bagasse and rice husks pretreated with AACC, suggesting that these lignins could be used as plasticizers to lower viscosity. Finally, the optimal DES to use for lignin extraction for a specific biomass will vary with the biomass. This work has attempted to characterize the lignin and derivatized lignin from waste biomass.

4.2 Future Work

More work should be done the reduce variability in the molecular weight values as the standard deviation of the molecular weight values were higher than is desirable. This points to each sample being structurally different and this becomes more evident for different biomass sources. The incomplete solubility of lignin after acetylation should also be further investigated. Benzoic acid should also be tried as an adjuvant with calculating the heating value to see what effect it has on the overall combustion and subsequent heating value (Shen et al., 2012). Also, using the lignins that had a wide molecular weight distribution as plasticizers in cement could identify a sustainable source for industrial use.

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