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Application of Lignin (Modified/Unmodified) to Cement and Observing Effects

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**APPLICATION OF LIGNIN (MODIFIED/UNMODIFIED) TO
CEMENT AND OBSERVING EFFECTS**

by

Ashique Ur Rahman Akond, BS

A Thesis Presented in Partial Fulfillment
of the Requirements of the Degree
Master of Science

COLLEGE OF ENGINEERING AND SCIENCE
LOUISIANA TECH UNIVERSITY

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Date

We hereby recommend that the thesis prepared under our supervision by
Ashique Ur Rahman Akond, BS
entitled Application of Lignin (Modified/Unmodified) to Cement and Observing
Effects

be accepted in partial fulfillment of the requirements for the Degree of
Master of Science in Molecular Science and Nanotechnology

Dr. Gergana Nestorova

Molecular Science and Nanotechnology

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ABSTRACT

Biomass of various types have been known to be important sources of energy or raw material for products in industries for centuries. Biomass have been proven to be cost effective as sources of suitable chemicals that can enhance many industrial processes. Lignin is one of many very valuable components extractable from biomass. Using lignin, modified or unmodified, can improve the sustainability of manufacturing processes. In this work, lignin was extracted from two different biomass, i.e. coffee chaff and sugarcane bagasse. Coffee chaff is the dried skins of coffee beans, the waste product from the roasting process. Sugarcane bagasse is the fibrous material remaining once the juice is extracted from the sugarcane. It can be dried and combusted as a solid biofuel. A deep eutectic solvent (DES) was used to extract lignin from these two biomass. DESs are hydrogen-bonded solvents that can extract lignin from biomass. They are safe, simple, cost effective and recyclable. In this study, the DES used was a two to one molar ratio of formic acid with choline chloride (FA:CC). The lignin extracted from the two biomass was added to cement to discover how they impacted the plasticity, porosity and compression strength of cement cylinders. In addition, commercially purchased sugarcane bagasse lignin was carboxymethylated and added to cement to investigate its effect on these properties.

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DEDICATION

This thesis is dedicated to the scientists and engineers who have labored to solve problems in people's lives.

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CHAPTER 1

INTRODUCTION

1.1 Lignin

1.1.1 General Overview

Lignin is a word derived from the latin word “lignum” which means wood (Schulz et al., 1857). It is a complex, natural, three-dimensional aromatic polymer. It is an underutilized substance produced by various industries, particularly the pulp and paper industry as black liquor. Black liquor is either combusted or discharged into the environment, polluting it, without making the best use from it (Nichols and Lien, 1993). Research has been focused on finding the best way to valorize lignin. Further investigation into different lignin end uses will allow it to be used in sustainable products and reduce the pollution caused by black liquor combustion.

1.1.2 Historical Background

Anselme Payen, a French chemist, first discovered lignin over 170 years ago. He treated wood with nitric acid and caustic soda and found two different products (Marton et al., 1966). One of them he called cellulose and the other, which was more wood-like, he called lignin (Philips et al., 1936). At that time, the nature and chemical structure of lignin was not very clear. The aromatic nature of lignin was highlighted by Bente and later Benedict and Bamberger found that, unlike cellulose, lignin was

composed of methoxyl groups (Benedict et al., 1890). Based on their experiments, Peter Klason postulated that lignin was made of coniferyl alcohol (Adler et al., 1977). Freudenberg in 1928 added that lignin was an amorphous and unordered material and the main connecting system would be carbon-carbon and ether linkages with the later preferentially alkyl aryl ether linkages (Chakar et al., 2004). In recent years, lignin's structural form in different types of plants has been studied, with many resulting publications.

1.1.3 Physical Structure

Lignin is an amorphous material with thermoplastic properties and has a glass transition temperature (T_g) that varies depending on the method of isolation, absorbed water, molecular weight and thermal history (Sarkanen et al., 1971). There are several interesting physical properties that are important in understanding lignin.

One of them is that it exhibits a T_g . It is very difficult to determine because lignin has broad heterogeneity in molecular weight. Wide-angle X-ray scattering (WAXS) results reveal a wide distribution of intermolecular distances; whereas infrared spectroscopy (IR) of lignin at different temperatures shows that intermolecular hydrogen bonding is broken and molecular motions are enhanced near the T_g (Hatakeyama et al., 1969). T_g shifts to higher temperature with increasing average molar mass. Many researchers have found that T_g varies from 90 °C to 150 °C (Irvine et al., 1984).

Thermal decomposition of lignin is another important topic and a considerable number of studies have been devoted to this field (Jakab et al., 1995). Lignin degradation is a complicated process involving competitive and consecutive reaction steps, due to its hindered structure. Lignin thermally decomposes over a broad temperature range because

the various oxygen-based functional groups have different thermal stabilities. The decomposition of lignin starts at a relatively low temperature, generally between 150 °C and 275°C. Finally, the complete rearrangement of the backbone, and hence releasing of volatiles, occurs at temperatures between 500 °C and 700 °C (Nassar et al., 2007).

1.1.4 Chemical Structure

Lignin plays a major role in woody plants, adding strength and structure to cell walls, controlling fluid flow and protecting against biochemical stresses by inhibiting enzymatic degradation of other components (Boerjan et al., 2003). Its chemical structure consists of phenylpropane units, originating from three aromatic alcohol precursors (monolignols), p-coumaryl, coniferyl and sinapyl alcohols (Dorrestijn et al., 2004). The phenolic substructures that originate from these monolignols are called p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) (Figure 1-1).

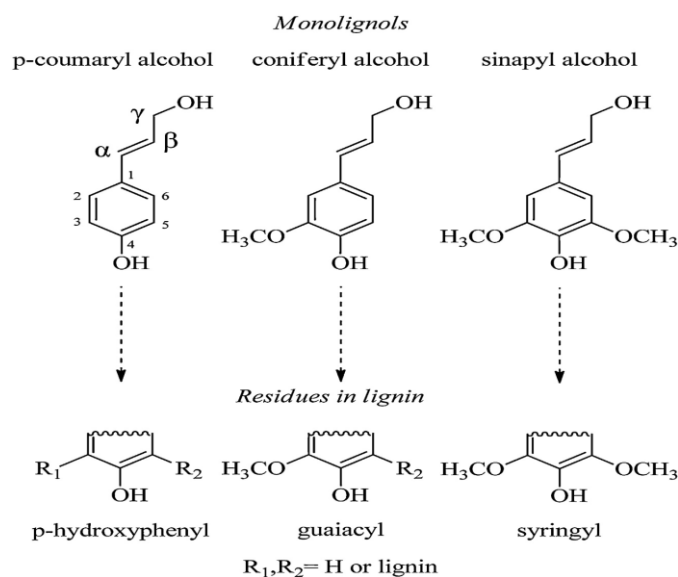


Figure 1-1: The three main precursors of lignin and their corresponding structures in lignin polymers (Dorrestijn et al., 2004)

During the biological lignification process the monolignol units are linked together via radical coupling reactions (Freudentberg et al., 1968) to form a complex three-dimensional molecular architecture that contains a great variety of bonds, with typically about 50% β -O-4 ether linkages (Ralph et al., 2004). The main characteristic linkages in a section of softwood lignin are depicted in Figure 2. Lignin composition and contents are influenced by the species and by the environment. Hardwood lignin consists basically of G and S units and trace of H units (Sarkanen et al., 1971) whereas softwood lignin mainly consists of G units with a low level of H units. Lignin from grasses, which are monocots, incorporate G and S units at comparable levels and more H units than dicots (Boerjan et al., 2003). Generally, lignin is recognized as a highly branched polymer with a variety of functional groups. The abundance of chemical sites offers different possibilities for chemical modifications and hint that lignin could play an effective role as a new chemical feedstock, particularly in the formation of aromatic compounds.

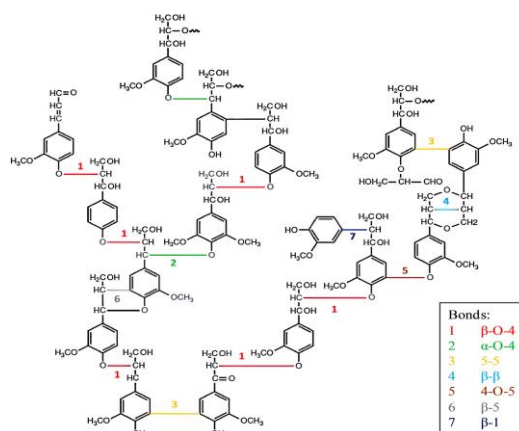


Figure 1-2: Main linkages in a softwood lignin (Windeisen and Wegener 2012)

1.1.5 Coffee Chaff

Coffee is a very popular drink around the world. The skin of coffee beans that comes off during roasting is called coffee chaff and is often considered to be a waste. Coffee chaff could be repurposed as an element for sustainable products. A sustainable product is something that gives suitable economic and social benefits, while protecting the environment. It has been shown previously that coffee chaff can be a good agent for producing wood plastic bonded boards (WPBB) (Aina et al.,2016). In their work, coffee chaff and ceiba pentandra (Kapok tree) were mixed with recycled low density polyethylene (rLDPE) particles in various proportions to make WPBB's of different densities. They reported that coffee chaff gave WPBB more strength than ceiba pentandra. In a separate study, it was shown that coffee chaff can be a successful building material in that it can absorb sound, reducing sound pollution (Ricciardi et al., 2017). In the present study, lignin from coffee chaff was mixed with cement to inspect its effects on the plasticity, porosity and the compressive strength of concrete.

1.1.6 Sugarcane Bagasse

Sugarcane bagasse is the dry pulp remainder after the juice has been extracted. It has often been considered a waste. It is abundantly produced in sugar factories because sugarcane is used to produce sugar. It can be combusted to produce heat and energy. Because it is sustainable while many other substances are not, studies have been made on its impact, performance and applications in its original form. Treating it with appropriate

chemicals and processes or combining it with other materials to make composites is another active area of investigation (Loh et al., 2013).

1.1.7 Extraction of Lignin

The pulp and paper industry produces lignin as a byproduct when separating cellulose from biomass. These facilities need high purity cellulose to produce paper, with a very low lignin content. Lignin is thus considered to be a low value waste, although it is useful for producing power to run facilities by firing it in a recovery boiler.

Approximately 20 billion tons of lignin byproduct is produced per year.

There are several methods by means of which lignin can be extracted, with the purity and chemical nature depending on the botanical source and the process of extraction (Vázquez et al., 1997). The figure below shows the classification into two main categories of commercially available processes (Vázquez et al., 1997).

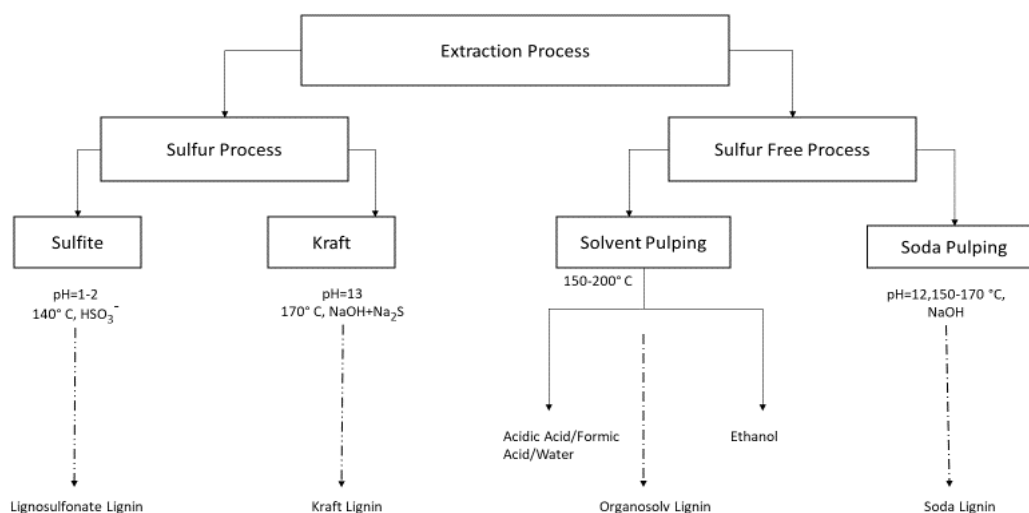


Figure 1-3: Different extraction process to separate lignin from biomass

1.1.7.1 Sulfur Lignin

Sulfur lignin can be of two types: Kraft lignin and lignosulfonate lignin. They are primarily produced in the pulp and paper industry. The Kraft process involves a mixture including sodium hydroxide (NaOH) and sodium sulfide (Na₂S), whereas the sulfite process involves cooking with aqueous sulfur dioxide (SO₂) and a base. The black liquor generated is then acidified to get sulfur lignin. Although Kraft lignin is produced in a high sulfur environment, its sulfur content is generally only 1-2%. It also has a high content of condensed structures and a high level of phenolic hydroxyl groups due to extensive cleavage of β-aryl bonds during cooking. The number average molar mass of Kraft lignin is relatively low, being between 1000-3000 g/mol (Baumberger et al., 2007).

Lignosulfonates contain a considerable amount of sulfur in the form of sulfonate groups present in the aliphatic chains. They are water soluble. They have higher molecular weight than Kraft lignin and a broad polydispersity index. For these reasons, they have various industrial applications, such as in binders, dispersing agents, surfactants, adhesives and cement additives.

1.1.7.2 Sulfur Free Lignin

Sulfur free lignins have relatively low molecular weight. They have interesting properties that make them an attractive source of aromatic compounds or low molar mass phenols. They can be divided into two major categories: lignins from solvent pulping (organosolv lignin) and lignins from alkaline pulping (soda lignin).

Organosolv lignin is generally the purest of lignins (Sannigrahi et al., 2009). It is very soluble in organic solvents, but not soluble in water because of its hydrophobicity. It

can be recovered from the solvent by precipitation, which usually involves changing some parameter such as pH, concentration or temperature (Vázquez et al., 1997).

Soda-based cooking methods are mostly used on annual plants such as straw, grass and bagasse, and to some extent hardwoods. Lignin extraction is based on hydrolytic cleavage of the native lignin, but it results in a chemically unmodified lignin compared to other lignin types. A famous example of this approach has been adopted by Granit SA (Orbe, Switzerland) as a specific method for precipitation of lignin from black liquor, by adjusting pH value with mineral acids. This method has been adapted from paper factories for the production of cellulose from annual plants or agricultural residual substances. Soda lignin can also have high silicate and nitrogen contents due to its extraction procedure (Lora 2008).

Successful introduction of lignin into the production of bio-based materials depends heavily on the structure and purity of lignin. The extraction process plays a significant factor in determining this. However, the abundant amount of lignin available has driven numerous research studies on how to valorize these lignins in various industries.

1.2 Deep Eutectic Solvent

Deep Eutectic Solvents (DESs) are now widely acknowledged as a new type of ionic liquid (IL), analogous because they share many characteristics and properties with them. The term ionic liquid and deep eutectic solvents have been used interchangeably, although it is necessary to point out that these are actually two different types of solvents. DESs are systems formed from a eutectic mixture of Lewis and Bronsted acids/bases that can contain a variety of anionic and/or cationic species, along with neutral species; in

contrast ILs are formed from systems composed of primarily one type of discrete anion and cation. It is illustrated here that although the physical properties of DESs are similar to ILs, their chemical properties suggest application areas that are significantly different.

The research into ILs has escalated in the last two decades ever since their potential for new chemical technologies were realized. In the period covered by this review, approximately 6000 journal articles have been published on ILs. Compared to classical ILs, the research into DES's is comparatively in its infancy. However, an increasing amount of effort is being applied to this field.

DESs contain large, nonsymmetric ions that have low lattice energy and hence low melting points. They are usually obtained by the complexation of a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD). The charge delocalization occurring through hydrogen bonding between, for example, a halide ion and the hydrogen-donor moiety is responsible for the decrease in the melting point of the mixture relative to the melting points of the individual components. A range of liquids formed from eutectic mixtures of salts and hydrogen bond donors have now been developed (Gorke et al., 2010). These liquids were termed deep eutectic solvents to differentiate them from ionic liquids that contain only discrete ions. The term DES refers to liquids close to the eutectic composition of the mixtures, i.e., the molar ratio of the components that gives the lowest melting point.

1.2.1 Properties of DES

1.2.1.1 Density, Viscosity, Conductivity and Surface Tension

While DESs and conventional ILs have different chemical properties, they have similar physical properties, in particular a potential to be tunable as solvents that can be

customized for a particular type of chemistry. Both types of solvents also exhibit a low vapor pressure, relatively wide liquid-range and nonflammability. DESs have several advantages over traditional ILs, such as their ease of preparation from relatively inexpensive components (the components themselves are toxicologically well-characterized, so they can be easily shipped for large scale processing). DESs are, however, in general less chemically inert. The production of DESs involves the simple mixing of the two components, generally with moderate heating. This maintains a comparatively low production cost with respect to conventional ILs (such as imidazolium-based liquids) and permits large scale applications. While the individual components of DESs tend to be individually well toxicologically characterized, there is very little information about the toxicological properties of the eutectic solvents themselves, and this needs to be further investigated by the scientific community. The term deep eutectic solvent was coined initially to describe type III eutectics but has subsequently been used to describe all eutectic mixtures. This is a logical approach, and although it includes all the early work on haloaluminates, will be adopted in this review (Wilkes 2002).

A method for predicting the density for DESs at different temperatures has been proposed (Shahbaz et al., 2011). The values of measured and predicted densities were compared, and the average of absolute relative percentage error (ARPE) for all the DESs tested was found to be 1.9%. The effect of salt to HBD molar ratio on ARPE in predicted DES densities was also investigated. The same group has also studied DESs formed from phosphonium based salts with different hydrogen bond donors (Kareem et al., 2010). Melting temperature, density, viscosity, pH, conductivity and dissolved oxygen content

were measured as a function of temperature. The authors found that the type of salt and HBD and the mole ratio of the compounds had a significant effect on the studied properties (Kareem et al., 2010).

It is generally observed that there is a good linear correlation between the molar conductivity and the fluidity. The same correlation would be expected with DESs. This is valid for a given electrolyte at infinite dilution in a range of solvents. Abbott showed, as a consequence of hole theory, that it is not the ions that limit charge transport but rather the holes (Abbott 2004). The refractive index of choline chloride (ChCl) based liquids with the hydrogen bond donors glycerol, ethylene glycol (EG) and 1,4-butanediol have been measured and compared to the predicted values using an atomic contribution method. The researchers reported that it was possible to predict the refractive indexes of these liquids using the atomic contribution method., and it was found that the refractive index lay between the values for the salt and the HBD (Wasserscheid and Welton 2008). Unsurprisingly, since there is a known relationship between viscosity and temperature, it has been shown that the electrical conductivity of DESs is also temperature dependent. The effective polarity of ChCl combined with four HBDs, 1,2-ethanediol, glycerol, urea and malonic acid has been predicted, and all four liquids were found to be fairly dipolar (Pandey et al., 2014).

1.2.1.2 Hole Theory and Ionicity

The use of deep eutectics has in some cases been limited by their increased viscosity and hence reduced conductivity when compared to aqueous electrolytes. Few studies have been carried out to comprehend the fluid properties of either conventional ILs or DESs. However, numerous models have been developed to account for the motion

of ions in high temperature ILs (molten salts), on the basis of the observation that the liquid volume and free volume of the liquid increase upon melting. The motion of ions in DESs has been rationalized using physical properties in hole theory (Abbott 2004). Hole theory assumes that, on melting, ionic material contains empty spaces that arise from thermally generated fluctuations in local density. The holes are of random size and location and undergo constant flux. The average size of the holes in molten salts is of similar dimensions to that of the corresponding ion, so it is relatively easy for a small ion to move into a vacant site, and accordingly, viscosity of the liquid is low. However, the average size of holes will be smaller in lower temperature systems, and coupled with a larger ion size this makes ion mobility difficult and explains high viscosities in these substances.

To quantify the viscosity of DESs it is assumed that cavities are not formed, but simply exist and move in the opposite direction to solvent ions/molecules. At any moment in time, a fluid will have a given distribution of cavity sizes, and an ion will only be able to move if there is an adjacent cavity volume of suitable dimension. Thus, only a fraction of the solvent molecules would be capable of moving, giving rise to the inherent viscosity of the fluid. The probability of finding an ion-sized hole in a high temperature salt is orders of magnitude larger than in its low temperature counterpart. If the limiting factor in the viscosity of liquids is assumed to be not the thermodynamics of hole formation, but the probability of vacancy location, then modeling fluidity becomes significantly easier. It has been shown that accurate prediction of conductivity in ILs and DESs can be achieved (Abbott 2004). Probability density and average size of free volumes within such liquids can be predicted using the Stokes–Einstein equation. The

application of hole theory to modeling viscosity helps with the design of low viscosity DESs. To obtain optimum mobility the ions must be relatively small, but the liquid must contain large cavities. This can be obtained by producing a liquid with low surface tension and hence larger voids. This theory is also valid for ILs with discrete anions.

The diffusion of modified ferrocenes in imidazolium ionic liquids, and analysis of the data showed that the diffusion coefficient did not obey the Stokes' equation, but rather there was a significant change in the calculated radius with temperature (Taylor, et al., 2011). This was explained in terms of the size of the holes in the liquid, and it was shown that mass transport occurred by a hopping mechanism. Later this was confirmed by D'Agostino et al, (2011) who described the first pulsed field gradient nuclear magnetic resonance (PEG-NMR) study of DESs (D'Agostino et al., 2011). The molecular equilibrium self-diffusion coefficient of both the choline cation and hydrogen bond donor was probed using a standard simulated echo PEG-NMR pulse sequence. The authors illustrated that increasing the temperature led to a weaker interaction between the choline cation and the corresponding HBD. The findings also highlighted that the molecular structure of the HBD can greatly affect the mobility of the whole system. In ChCl:EG, ChCl:glycerol, and ChCl:urea the choline cation diffuses more slowly than the associated HBD, reflecting the trend of molecular size and molecular weight. The opposite behavior is observed for ChCl:malonic acid, where the malonic acid diffuses more slowly than the choline cation; the authors attributed this to the formation of extensive dimer chains between malonic acid molecules, restricting the mobility of the whole system at low temperature.

1.2.1.3 Speciation

The ionic nature and relatively high polarity of DESs mean that many ionic species, such as metal salts, show high solubility. One of the key questions when considering the reactivity of a metal in a DES is the species that form upon dissolution. Metal ions being generally Lewis acidic will complex with Lewis or Brønsted bases to form a variety of complexes. In aqueous solvents, the chemistry of H^+ and OH^- dominate the species formed in solution, the redox properties and the solubility of metals. The study of metal ion speciation in DESs has only started recently; unfortunately, the systems are more complex than aqueous solutions because of the differing Lewis basicities of the anions and composition of the eutectic. It is vital to understand speciation in DESs when trying to determine the mechanisms of nucleation and growth of metallic coatings, because the number and binding constants of the ligands determine the detailed mechanistic steps associated with electrochemical reduction. One of the reasons speciation is poorly understood is the difficulty in acquiring quantitative structural data. Most metals form ionic complexes that are difficult or impossible to crystallize from solution, and of course evaporation of the solvent is not possible. A series of in situ techniques are required to assimilate metal ligation in solution (Haerens et al., 2009).

X-ray absorption fine structure (EXAFS) arises from a modulation in intensity of the X-ray absorption edge by interference with photoelectrons backscattered from neighboring atoms. Fourier transformation provides a radial distribution function in real space within a radius of approximately 600 pm. EXAFS is element specific and shows the local arrangement around the excited element, even for low concentrations. To date EXAFS has been used to study $ZnCl_2$, $CuCl_2$, and $AgCl$ in both $ChCl:EG$ and $ChCl:urea$

DESs. It was found that ZnCl_4^{2-} and CuCl_4^{2-} were present in the former solutions whereas the latter liquid contained a mixture of AgCl^{2-} and AgCl_3^{2-} . While these results are intuitively consistent with the high Cl^- ion concentration (ca. 4.8 M) in both of these liquids, it suggests that the coordination chemistry of the zinc ions at the electrode surface controls the deposition mechanism and further complicates the elucidation of these processes. A study by Rodriguez et al. (2007) used soft X-ray absorption spectroscopy to probe solute–solvent interactions in ChCl:urea mixtures with a nitrate salt (Rodrigues et al., 2007). The authors experienced significant problems with the signal of the solvent, but were able to detect solute signals, and see spectral changes attributed to solvent–solute interactions. The differential spectrum obtained from subtraction of the spectra of sodium nitrate dissolved in DES with pure DES was almost the same of that of pure nitrate indicating no strong interaction between the choline cation and nitrate anion (Rodrigues et al., 2007).

1.2.1.4 Green Credentials

Ionic liquids have been described as “green solvents” largely because of their low vapor pressure. However, this is a misnomer, and in recent years the toxicity and biotoxicity of ILs have been investigated, proving that they are not inherently “green” (Deetlefs and Seddon, 2010). DESs may offer a “greener” alternative to many traditional ILs, but they are also not by definition “green”. With the above formulations describing more than 10 liquids, some DESs will be inherently nontoxic, being composed of benign constituents. Types I, II, and IV eutectics all contain metal salts with their innate toxicity; however, type III eutectics can encompass a variety of amides and polyols such as urea,

glycerol, fructose and erythritol, which have low inherent toxicity (some formulations can even be produced using food grade ingredients).

To date most of the applications of DESs have been focused in the area of metal finishing, and relative toxicity should be compared with the aqueous mineral acids that they seek to replace. A study on the environmental impact of the DES based on choline chloride and EG in electroplating applications has been carried out (Haerens et al., 2009). Both components are not harmful to the environment, and both are readily biodegradable, with the resultant DES also readily biodegradable. Hence, the main environmental impact for the process was found to be related to the presence of heavy metals in rinsing solutions and products formed during electrolysis due to incomplete current efficiency at the cathode and anode reactions. After surface treatment in the DES electroplating bath, a film of the bath solution will remain on the parts and on the rack or barrel. The bath solution also remains in cavities or gaps and is transferred into subsequent baths. Process solution lost in this way is termed drag-out. Drag-out leads to the consumption of the plating bath and is a source of pollutants in the rinse water. It was found that drag-out was the parameter with the greatest influence on the environmental impact of the process, as it was three times higher compared to classical solutions due to the higher viscosity of the DES (Haerens et al., 2009). A range of chlorinated products such as chloromethane, dichloromethane, and chloroform were also detected, though chlorine gas evolution was not observed at the anode. The presence of the chlorinated products was ascribed to the existence of Cl^{3-} in the solution, which was observed photometrically. The presence of chlorinated products did give rise to a large environmental impact; however, it was shown that the presence of chlorinate compounds could be reduced by the addition of

water and that formation of 2-methyl-1,3-dioxolane could be reduced by the addition of sacrificial agents. Sacrificial agents are chemical agents that are used to produce something specific, but which themselves have little value.

DESs do have lower vapor pressures than most molecular solvents and tend to result in decreased emissions to the atmosphere; however, they are partly miscible with water and could inevitably end up in the aqueous environment. For DESs to be truly “green” a method for recycling needs to be ascertained, along with methods to remove DESs from aqueous environments. The use of pressure driven membrane processes, nanofiltration, reverse osmosis and pervaporation have been investigated as possible techniques for the recycling of DES. In electrodeposition processes, DESs are likely to end up in the rinse water; in other applications, DESs will have to be separated from water or solvents. These applications include the production of zeolites, Suzuki coupling reactions and cellulose processing (Lindberg et al., 2010). Separation of water from a DES could be achieved by evaporation; however, this is very energy consuming and requires higher temperatures at which some DESs may decompose.

Although components of a DES can be nontoxic and of low environmental impact, it does not necessarily follow that mixtures of these components will be non toxic and inherently “green”. This is underpinned by the fact the DESs have special properties that neither of the individual components have. The toxicity and cytotoxicity of choline chloride with the HBDs glycerine, EG, triEG, and urea have been investigated. They found that the cytotoxicity of the DESs was much higher than their individual components and the toxicity and cytotoxicity varied depending on the structure of the

components (Haerens et al., 2009). It is clear that more investigation is needed into the toxicity of DESs before they can truly be claimed as nontoxic and biodegradable.

1.2.2 Deep Eutectic Solvent Application

An emerging research area for DESs is their use in biotransformations. A biotransformation is a chemical modification made by an organism or enzyme on a chemical compound, which is vital to our survival as it allows the body to transform absorbed nutrients (e.g. food, oxygen) into substances that we require to function. The body also uses biotransformation or metabolism to turn an absorbed drug into the active agent or to convert toxins in the body into less harmful substances that can be excreted. Traditionally, biotransformations have been performed in aqueous solvents; however, biocatalysis has also been attempted in polar organic solvents such as acetone, methanol or dimethyl sulfoxide (DMSO), although the polar organic solvents regularly denature enzymes. Replacing polar organic solvents with DESs allows substrates to dissolve without deactivating enzymes. DESs can be used in three different ways: as a cosolvent with water to help nonpolar substrates dissolve in aqueous solution, as a second phase in a water-DES mixture, or as a nonvolatile replacement for nonaqueous solvent. Deep eutectics could potentially be a technically and economically viable alternative to organic solvents (Gorke et al., 2010).

The first proof-of-concept concerning the use of DESs in biotransformations only appeared in 2008 (Gorke et al., 2008). The reactions studied so far have involved lipase-catalyzed processes such as transesterification (Zhao et al., 2011), aminolysis, epoxide hydrolysis (Lindberg et al., 2010), n-alkylation of aromatic primary amines (Singh et al., 2011), and Knoevenagel condensation reactions (Sonawane et al., 2010). These have

generally exhibited rates and enantioselectivities comparable to or higher than those reported for conventional organic solvents. It has recently been discussed in the literature whether naturally forming DESs can provide the missing link in understanding cellular metabolism and physiology (Choi et al., 2011).

Biotransformations using microorganisms are limited in any nonaqueous solvent, and adding water unfortunately modifies DESs, breaking the electrostatic interactions among the components. To overcome this, freeze-dried whole cells have been incorporated in a DES, preserving the bacteria integrity and viability. In 2008, Gutierrez et al. (2008) initially published the preparation of a DES in its pure state through the freeze-drying of aqueous solutions of the individual DES counterparts, and went on to explore the suitability of freeze-drying to incorporate organic self-assemblies in the DES with the full preservation of their self-assembled structure (Gutierrez et al., 2009).

1.2.2.1 Transformations of Unprotected Sugars, Cellulose and Starch

Transformations of certain organic compounds such as unprotected sugars and cellulose can also be carried out advantageously in these liquids. The selective O-acetylation of sugar and cellulose (Abbott et al., 2005) has been reported, as well as the cationic functionalization of cellulose (Abbott et al., 2006). The O-acetylation of carbohydrates is used for the protection of hydroxyl groups and for the purification and structural elucidation of natural products. DESs based on ZnCl_2 and ChCl are effective at carrying out O-acetylation reactions on a number of monosaccharides and cellulose. Per-O-acetylation was exclusively observed with monosaccharides and for low molecular weight polymers. Partial acetylation of cellulose was shown to be possible with some control over the degree of modification. The efficient cationic functionalization of

cellulose was demonstrated in ChCl:urea DES, which acts as both solvent and reagent. It was shown that all the available hydroxyl groups on the cellulose had been modified. Zhao et al. (2011) have reported the rapid decrystallization of cellulose in DESs (Zhao et al., 2011). The authors discuss the effect of additives and the recycling of DESs. Starch is a biopolymer used in industry as a coating in paper, textiles and carpets, and in binders, adhesives, absorbants and encapsulators. It is often modified to improve its end-use properties; however, the only solvent it is soluble in is DMSO, and then only sparingly. Starch has been found to be soluble in ChCl:oxalic acid and ChCl:ZnCl₂, and as a result, these DESs could be used as a solvent for the chemical modification of starch (Biswas et al., 2006).

DESs have also been investigated for their suitability as plasticizers for starch and cellulose acetate (Ramesh et al., 2012). DESs based on ChCl are good candidates for starch modification because they interact strongly with the OH groups of the glycosidic units, decreasing chain interactions and hence plasticizing the polymer. They can also wet the surface of individual grains and bind them together. The DES found to have the best plasticizing properties was ChCl:urea. ChCl:urea has been used to suppress the crystallinity of corn starch and cellulose acetate in a polymer electrolyte containing lithium bis(trifluoromethanesulfonyl)imide, LiTFSI. The highest ionic conductivity for corn starch was obtained from a sample containing 80 wt % of DES, with a calculated conductivity value of $1.04 \times 10^{-3} \text{ S cm}^{-1}$ in comparison with a sample containing 60 wt % DES for cellulose acetate, giving an ionic conductivity of $2.61 \times 10^{-3} \text{ S cm}^{-1}$ (Ramesh et al., 2012).

1.2.2.2 Purifying and Manufacturing Biodiesel

There are many benefits of producing biodiesel as an alternative fuel: its synthesis from a natural product means that it is a carbon neutral fuel; it produces significantly fewer particulates than conventional diesel fuel with no sulfurous emissions; and it can be used pure or blended with mineral diesel in most modern compression engines. The manufacturing process for biodiesel is similar for any natural product oil feedstock: triglyceride oil extracted from the plant is transesterified into alkyl esters using a catalyst to yield three mol of ester and one mol of glycerol per mol of triglyceride used. The glycerol is an unwanted byproduct and must be removed before the biodiesel can be used as a fuel, as the viscosity of the glycerol present impedes the high pressure injection system of a modern diesel engine. The major stumbling block to the widespread use of biodiesel is that it is cheaper to drill and refine mineral diesel oil than to grow, extract, transesterify and purify biodiesel using conventional methods of adsorption over silica membrane reactors or the addition of lime and phosphoric acid. The use of DESs in the synthesis of biodiesel have also recently become a subject of a review (Zhao et al., 2012).

In 2007, Abbott et al. successfully extracted excess glycerol from biodiesel in the presence of KOH using a Lewis basic mixture with a ratio of salt:2 glycerol using a DES (ChCl:glycerol, 1:1) (Abbott et al., 2007). A 25% portion of the ChCl was subsequently recovered from the mixture by adding 1- butanol as a liquid cosolvent. A collaboration between the University of Malaya, Malaysia; the King Saud University, Saudi Arabia; and Sultan Qaboos University, Oman has investigated the findings of Abbott et al. (2007) confirming that the optimum molar ratio for the ChCl:glycerol DES is 1:1 and that the most glycerol was extracted using a 1:1 mixture of biodiesel:DES (Hayyan et al., 2010).

The group also found that two different DESs, consisting of ChCl and the hydrogen bond donor EG or 2,2,2-trifluoroacetamide (Shabnaz et al., 2010), were also successful in extracting glycerol from biodiesel. Recently, they have reported that ChCl based DESs with EG and triethylene as hydrogen bond donors were successful in removing all free glycerol from palm-oil-based biodiesel (Shabnaz et al., 2011), although to date no further advances have been reported by this collaboration on recovering the glycerol from the DES. ChCl:EG and ChCl:2,2,2-trifluoroacetamide have also been proven to successfully remove glycerol from palm-oil-based biodiesel (Shahbaz et al., 2013).

The successful recovery of glycerol from biodiesel would, however, pose a new conundrum: Can the recovered glycerol be put to use? Glycerol has some uses as viscosity modifiers and freezing point suppressants; however, with an annual production in excess of 1 million tonnes the market is saturated. Glycerol is poorly combustible so it cannot be used as a fuel and is regarded by many as a waste product. One solution to this problem has been reported by Abbott et al. (2011), who have developed a sustainable way of preparing nontoxic tunable DESs with glycerol as the hydrogen bond donor (Abbott et al., 2011). Eutectic mixtures of glycerol with ChCl were shown to circumvent some of the difficulties associated with using glycerol as a solvent, such as high viscosity and high melting point. The application of these liquids to the esterification of glycerol was used to demonstrate the ability to tune a reaction with the quaternary ammonium acting as a quasi-protecting group. A feature article published by a group from the Universidad de Oviedo, Spain, reviewed attempts to increase the worth of glycerol extracted from biodiesel as an environmentally friendly reaction medium for synthetic organic chemistry (Diaz et al., 2011).

In an alternative approach, ChCl and choline acetate based deep eutectics have been investigated as suitable solvents for lipase activation and enzymatic preparation of biodiesel. ChCl:glycerol has also been used as a solvent for the enzymatic preparation of biodiesel from soybean oil. ChCl:glycerol has been used as the activator and solvent in the CaO-catalyzed transesterification of rapeseed oil to produce biodiesel (Huang et al. 2013).

The similarity in physical properties between DESs and ILs suggests that they belong in the same class of liquid distinct from molecular liquids; yet, the disparity in chemical properties between the liquids means that to date DESs have found very different application fields compared to ILs. The metal finishing industry is being restricted by legislation, toxicity issues and cost; DESs offer a viable alternative to existing technologies, and hence, the application and scale-up of these processes have received considerable attention. While research into DESs has mainly focused on their application in metal finishing, DESs are beginning to be used in various synthetic applications; the limited reactions that have been investigated prove the potential of DESs in this area. Thus far, only a narrow range of DESs have been utilized: the future offers significant potential to expand the types of salts and hydrogen bond donors that are used and hence further increase the applications of these solvents.

1.3 Carboxymethylation of Lignin

Lignin produced in the pulp and paper industry is usually considered to be waste material and thought of as no more useful than fuel for generating power. When lignin is put into industrial processes, its usefulness is often hindered or limited because of its

inability to dissolve in water. Many modifications of lignin have been considered and tried such as sulfonation, oxidation and copolymerization. However, due to problematic reaction conditions, such as high temperature and the need for expensive catalysts and organic solvents, these modifications have not proven to be feasible. One modification, carboxymethylation of lignin, does not involve any of these complications.

Carboxymethylated lignin products can be put into various uses, such as in adhesives, dispersants or stabilizing agents.

1.4 Fourier Transform Infrared Spectra (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic (and in some cases inorganic) materials. This technique measures the absorption of infrared radiation by the sample material versus wavelength. The infrared absorption bands can identify molecular components and structures.

When a material is irradiated with infrared radiation, absorbed IR radiation usually excites molecular bonds into a higher vibrational state. The wavelength of light absorbed by bonds in a particular molecule is a function of the energy difference between the at-rest and excited vibrational states. The wavelengths that are absorbed by the sample are characteristic of its molecular structure.

The FTIR spectrometer uses an interferometer to modulate the wavelength from a broadband infrared source. A detector measures the intensity of transmitted or reflected light as a function of its wavelength. The signal obtained from the detector is an interferogram, which must be analyzed with a computer using Fourier transforms to obtain a single-beam infrared spectrum. The FTIR spectra are usually presented as plots of intensity versus wavenumber (in cm^{-1}). Wavenumber is the reciprocal of the

wavelength. The intensity can be plotted as the percentage of light transmittance or absorbance at each wavenumber.

1.5 Cement Compression Strength

Compressive strength is the ability of a surface or a structure to carry the loads on its surface without any crack or deflection. A material under compression force tends to reduce in size. The compressive strength of a hardened cement paste (subsequently referred to as cement) cylinder is indicative of many characteristics of the cement. Compressive strength of cement depends on many factors such as water cement ratio, cement strength, quality of cement material etc. The aim should always be at making cement that has large compressive strength.

1.6 Cement Porosity

Porosity is the number of pores in a material, in this case in cement. The porosity of cement has influence on its properties. In highly porous materials, moisture absorption is high and they may crack with freeze/thaw cycles easily. In structures that are less porous, moisture absorption is low, and cracking is reduced.

CHAPTER 2

MATERIALS AND METHODS

2.1 Raw Materials and Chemicals

Coffee chaff was donated from Orleans Coffee (Kenner, LA, USA). Sugarcane bagasse and rice husks were harvested in Louisiana and obtained from Falcon Rice Mill (Crowley, LA, USA) and Lula Westfield (Paincourtville, LA, USA), respectively. Choline chloride (ChCl) powder (Bioreagent, suitable for cell culture, $\geq 98\%$), formic acid (reagent grade, $\geq 95\%$) were purchased from Duda Energy LLC. Monochloroacetic acid was purchased from Alfa Aesar (Ward Hill, MA, USA). Sodium hydroxide was bought from Sigma-Aldrich (St. Louis, MO, USA). The pH meter (ORION STAR A11) was bought from Thermo Scientific (Waltham, MA, USA). The vacuum dryer oven was purchased from Across International (Accu Temp – 09s, Livingston, NJ, USA).

2.2 Synthesis of DES

Formic acid (HCOOH) and ChCl (C₅H₁₄ClNO) were combined to make FA:CC deep eutectic solvent in a 2:1 molar ratio. In a water bath at 60 °C, they were mixed for 20 minutes with stirring until the mixture was as clear as water.

2.3 Drying of Biomass for Pretreatment

Coffee chaff and sugarcane bagasse were placed in an oven dryer at 105 °C for about 24 hours. Then, they were meshed to a diameter of between number 14 mesh and 25 mesh. Biomass particle size was thus about 1 mm.

2.4 Pretreatment of Biomass with DES

Dried and sieved biomass was mixed with DES by means of a magnetic stirrer in an oil bath at 152°C ±2°C. There was a condenser at the top of the conical flask, sealing the opening of the conical flask and condensing and sending back any vaporized DES solvent. Reaction time was 2 hours and 15 minutes for each biomass. The mass of the biomass was 30 g and the mass of the DES was 300 g for a 1:10 mass ratio.

2.5 Separation of Lignin

After the reaction, the conical flask was allowed to cool down to room temperature. Solids were separated from DES with dissolved biomass components by vacuum filtration. All of the filtration was done using membranes that were dried for 30 minutes at 110 °C prior to use. Ethanol (25-30 ml) was added to the remaining solids and was put on a magnetic stirrer for 7-10 minutes. After that the biomass was filtered again to separate unreacted biomass from dissolved components. The flask then contained a filtrate with a mixture of dissolved biomass components (lignin-rich, and subsequently

called lignin). Water of volume ~1750 ml was added to the lignin-alcohol mixture and the mixture remained at room temperature for ~24 hours.

Several hours into the wait of 24 hours, the mixture of lignin-water-alcohol was hand shaken so that lignin mixed with the liquid. Eventually, the lignin settled at the bottom of the flask, leaving clear liquid above. After 24 hours, the clear liquid above the precipitate at the bottom was carefully decanted with very little loss of lignin, leaving only a lignin-liquid mixture at the bottom. That lignin-liquid mixture was subjected to vacuum filtration and solid lignin was separated from the DES-water-ethanol filtrate. The lignin was collected and stored in a vacuum oven for about 24 hours at 60 °C. The conversion ratio was around 1/6 for each biomass/lignin, that is, 1 g of lignin was found from 6 g of biomass for each biomass. After that each biomass was ground with mortar and pestle and powdered so that they could pass through an 80 mesh, giving a particle size of 0.177 mm or less. Ground lignin was then stored in a plastic bag.

2.6 Carboxymethylation of Lignin

Carboxymethylation was done on a commercial sugarcane bagasse lignin (BOC Sciences, Shirley, NY, USA). Lignin (240 g) was placed in a conical flask, equipped with a magnetic stirrer. Sodium hydroxide (20 wt%) was prepared by mixing 120 g solid NaOH with 480 ml of deionized water. Monochloroacetic acid solution (37.5 wt%) was made by adding 144.0 g of monochloroacetic acid to 240 ml (300 g) of deionized water. The NaOH solution was added to the lignin and reacted in a water bath at 70 °C for 30 minutes so that the lignin would be dissolved in NaOH. Then monochloroacetic acid solution was added dropwise to the flask for 30 minutes. After that, the solution was allowed to react for 90 more minutes. After the reaction, pH of the solution was found to

be around 10.50. pH of the solution was adjusted by adding hydrochloric acid dropwise to the solution until it reached 4.40 ± 0.20 . Then it was subjected to vacuum filtration. As a filtered product, the carboxymethylated product was found and was washed with ethanol several times. Then it was dried in a drier for one day at $70\text{ }^{\circ}\text{C}$. It was ground by mortar and pestle to pass through a number 80 mesh and stored in a plastic bag. Approximately 30 g of carboxymethylated lignin was made.

2.7 FTIR Analysis

A Mattson Genesis FTIR II (Mattson Technology, Fremont, CA, USA) was used to obtain the spectra of biomass samples. KBr pellets were produced in this procedure. One mg of sample was mixed with 100 mg of KBr and a pellet was made by applying pressure. On each sample, 32 scans were run with a resolution of 2 cm^{-1} from wavenumber $3000\text{ to }800\text{ cm}^{-1}$. FTIR analysis was performed on coffee chaff lignin, sugarcane bagasse lignin, rice husk lignin, corn stover lignin, commercially purchased sugarcane bagasse lignin and the carboxymethylated product of the commercial sugarcane bagasse lignin. Data analysis of the spectra was done using OMNIC software.

2.8 Cement Batch Procedure

At first, saltwater was prepared. Salt (34.65 g of NaCl) was mixed with 990 g of water to make a saltwater of 3.4 wt% concentration. Saltwater was used in this experiment because it is more sustainable globally, especially in places near the ocean, so that potable water is not needed. Hardened cement paste (subsequently referred to as cement) has been used in this study because the properties of concrete with added aggregate can depend significantly on the orientation and character of the aggregate used. Cement (2193.4 g) was placed in a Kitchen Aid 600™ mixer bowl. Density of the cement

was 2.402 g/cm^3 . The lignin (6.6 g) was added to the cement and mixed very well. A squirt bottle was filled with saltwater a little more than halfway and the rest of the water was poured into the bowl. Mixing was initiated. Whenever the mixture became thick and dry, water from the squirt bottle was squirted into the mixing bowl so it would not dry out and more importantly, so cement mixture would not stick to the stirrer. After all water in the bottle had been added to the mixing bowl, the mixture was then stirred for five minutes more before slump testing. The cement paste was then poured into the cylindrical molds, filling one third at a time and tamping 25 times with a 30.48 cm (12 inches) long by 0.9525 cm (3/8 inch) diameter steel rod as per ASTM C192. The molds were cut all the way down the side and taped tightly so that the cement paste would not leak out of the mold and also the cement cylinders could be taken out of the molds without damaging the molds, so that they could be used again. Six molds were filled, each time filling 1/3 part of each mold, prior to tamping, which was performed to make sure that there were no bubbles. The cement paste sat in the molds for 24 hours to harden. After 24 hours they were taken out of the molds and put in calcium hydroxide “lime” water for 28 days. Lime water was made by adding 10 g calcium hydroxide into 5 liters of water (2g/L). After 28 days compression testing was carried out. The cement batching procedure was carried out for cement without any plasticizer, cement with lignin as plasticizer and cement with carboxymethylated lignin as a plasticizer.

2.9 Slump Test, Compression Test, Porosity Test

A mini-cone slump test was done on the cement paste right after batching. A mini-slump cone was 3-D printed, 5.7 cm in height, 1.9 cm inner top diameter, and 3.8 cm inner lower diameter. This test involves a slump base. This slump base has coordinate

axes drawn on it. One slump cone was sat on the slump board and on it another was set reversely so that their openings match and the top cone serves as a funnel. Cement was poured into the slump cones so that both of them were filled to the top. The excess cement paste at the opening of the bottom slump cone was then scraped off. The bottom slump cone was pulled vertically upwards allowing the cement paste to spread over the slump board. It spread in all directions and created some kind of a circular/elliptical shape. Distance covered in both positive and negative x and y axis was recorded. These diameters on the X and Y axes were used to calculate the area of the cement oval, which is $\pi \times (X \text{ diameter}/2) \times (Y \text{ diameter}/2)$, after slump cone removal.

Compression testing was conducted 28 days after the cement batching (ASTM C39). A load was applied at 241 kPa/s until there was a crack on the cement blocks. A sample break of 85% was used. That means if a fracture in the cement cylinder caused the stress on the cylinder to fall below 85% of the load being applied then the machine would stop and display the result (Travis et al., 2020).

After the compression test, the broken cement pieces were collected and porosity tests were performed on them. These were simple experiments in which each broken piece was placed in a water bath for a whole day and then placed in a 105 °C dryer for 4 consecutive days. Mass was recorded at each step of the experiment. Porosity was measured in terms of the water absorbed by the cement cylinders.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Mass Yield from DES Pretreatment

Around 120 g of coffee chaff was pretreated with the ultimate purpose of extracting lignin. Around 20 g of lignin was found with a yield of 1/6. Around 90 g of sugarcane was subjected to the same process and around 15 g of lignin was extracted, giving a similar yield.

3.2 Plasticity Effect of Lignin on Cement

To measure plasticity of the cement, slump tests were performed. Table 3-1 and Figure 3-1 demonstrate the results found. Lignin or carboxymethylated lignin impacted the plasticity or fluidity of cement in different ways. Lignin increased it while carboxymethylated lignin did not. While carboxymethylated lignin reduced the area of the cement paste in slump test by 20%, lignin from sugarcane bagasse and coffee chaff increased it by from 67% to 112%. Coffee chaff lignin and sugarcane bagasse lignin increased the plasticity of cement paste considerably when used at 0.3% as a plasticizer, while carboxymethylated lignin decreased the plasticity of cement to some extent when added at 2% and 4% plasticizer. Given the difficulties construction workers face with cement paste hardening too quickly or requiring too much water, adding lignin to it seems like a very efficient solution.

The reason of the increased plasticity could be attributed to the relation viscosity has with molecular weight distribution. A wide molecular weight substance tends to have lower viscosity (Saba et al., 2018). Because coffee chaff lignin and sugarcane bagasse lignin have a wide range of molecular weight, they decrease the viscosity of the cement paste and increase plasticity (Owen et al., 2020).

Table 3-1: Workability as measured by mini-slump test of various cement mixtures

Batched Material	Diameter on X Axis	Diameter on Y Axis	Average of Diameters	Area (in inch ²)	Area (in cm ²)
Cement Without Plasticizer (1)	2.75	2.50	2.62	5.41	34.90
Cement Without Plasticizer (2)	2.90	2.75	2.82	6.26	40.43
Cement With Sugarcane Bagasse Lignin as Plasticizer	4.00	3.65	3.82	11.49	74.12
Cement With Coffee Chaff Lignin as Plasticizer	3.60	3.70	3.65	10.46	67.50
Cement With Carboxymethylated Lignin as Plasticizer (2%)	2.30	2.25	2.27	4.06	26.21
Cement With Carboxymethylated Lignin as Plasticizer (4%)	2.35	2.35	2.35	4.33	27.93

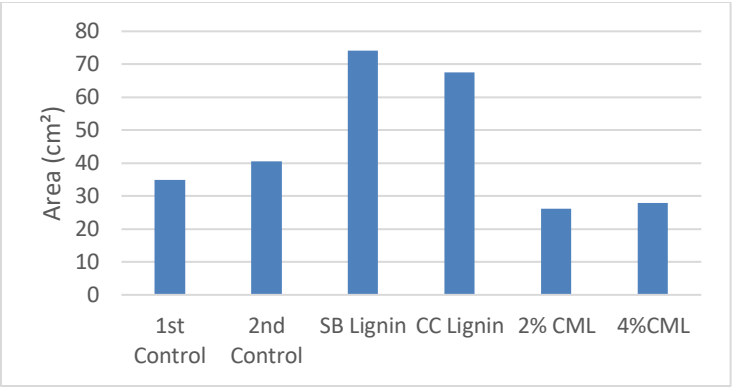


Figure 3-1: Slump areas for the different cement batches.

3.3 Compression Testing on Cement Block

Figure 3-2: shows the effect of different types of lignin on the compression strength of cement.

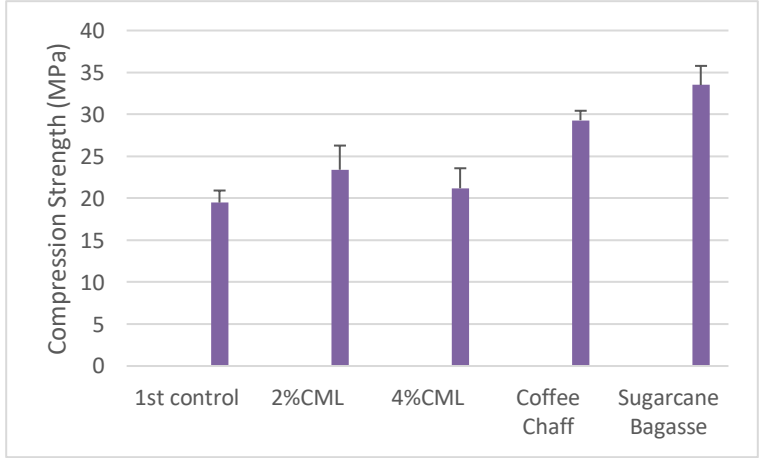


Figure 3-2: Compression strength of different cement batches, with standard error bars shown.

As shown in Figure 3-2, both 2% and 4% CML appeared to increase the compression strength of cement in different batches to some degree. On average, 2% CML increased the compression strength by 21% and 4% CML by 8.7%. No definite

conclusions can be drawn due to the variation in compression testing results for 2% and 4% CML compared to control. However, addition of coffee chaff lignin and sugarcane bagasse lignin increased the compressive strength of cement quite significantly, especially sugarcane bagasse lignin. Coffee chaff lignin increased the compressive strength of cement by 50%. Sugarcane bagasse lignin increased it by 72%, even more than coffee chaff lignin. Adding 0.3 wt% of the two types of lignin had a large influence on the compression strength of cement, especially sugarcane bagasse lignin.

The compressive strength of a cement block tends to be increased with the decrease of water in the cement water mixture. When plasticizers are added to the cement they can improve the quality of the cement with the same water content. This may be because they are constituted of organic substances or a combination of organic and inorganic substances (Dodson et al., 1990). The reason that coffee chaff lignin, sugarcane bagasse lignin, and carboxymethylated lignin increased the compressive strength of cement blocks could be due to the fact that they are organic in nature.

3.4 Porosity Test

Porosity was 21.51% for coffee chaff lignin and 19.95% for sugarcane bagasse lignin. The porosity of the control with no lignin was 22.60% with a standard error of 0.10%. So, porosity was slightly less with sugarcane bagasse lignin addition and coffee chaff lignin addition compared to the control. Since lower porosity is more desirable, adding these lignins was found to be beneficial. Sugarcane bagasse lignin addition gave slightly lower porosity compared to coffee chaff lignin addition. Thus,

adding sugarcane bagasse lignin as a plasticizer is preferable in enhancing both compressive strength and porosity.

The reason that porosity decreased after adding lignin could be due to the fact that the collective volume of pores and voids in the cement block is less after lignin is added. It might be attributed to the fact that lignin is a very dense structure. Improved cement mixing from the wide molecular weight distribution of the lignins may also have reduced the porosity.

Table 3-2 shows the data from the porosity tests that were conducted. Porosity stabilized after three days and thus a three-day measurement was taken for mass decrease porosity values.

Table 3-2: Mass data in porosity experiments

Type of Lignin	Soaked Mass	Dried Mass after One Day	Dried Mass after Two Days	Dried Mass after Three Days	Dried Mass after Four Days	Porosity
Coffee chaff Lignin	6.88	5.64	5.27	5.42	5.40	21.22%
Sugarcane Bagasse Lignin	9.77	7.99	7.79	7.82	7.82	19.96%

3.4 FTIR Analysis

FTIR spectra of four biomass are shown in Figures 3-3 through 3-8. Although all of them are similar, there are some differences. There are several vibrations in the spectra that are indications of the specimen being lignin rich. For example, the 858 cm^{-1} vibration indicates the vibration of C-H bonds in association with aromatic groups. The 1515 cm^{-1} vibration indicates aromatic ring C-C stretching vibrations. The 1718 cm^{-1} vibration indicates a stretching vibration of C=O bonds at the β location and in the -COOH group. While each of the four biomass has most of them, coffee chaff lignin does not have the 1600 cm^{-1} vibration. The vibrations indicating cellulose, which also appear in every lignin except for rice husk lignin, indicate that they are not totally pure. The relative intensity of an FTIR vibration tends to indicate the concentration of the atom or group. So, the higher the intensity, the more frequently that atom or group is found in the substance. The reason for having several cellulose vibrations can be attributed to incomplete separation.

From the FTIR results it can be concluded that the extraction of lignin was reasonable, but not exactly flawless. With rice husk, the extraction of lignin probably was the most efficient while with the other three biomass the extraction was sufficient but not necessarily optimal. The spectrum of rice husk lignin had all the four characteristic vibrations, and two of the vibrations had large areas with the other two vibrations having relatively large areas. With spectra for corn stover and sugarcane bagasse lignins, all the four characteristic vibrations was found, but the areas were not comparatively large. Coffee chaff lignin's spectrum was missing one of the characteristic vibrations (1600 cm^{-1}). In terms of evidence for cellulose content, rice

husk lignin appeared pure, because it did not have even one cellulose vibration in its spectrum. Coffee chaff lignin and corn stover lignin had one cellulose vibration present in their FTIR spectra. Sugarcane bagasse lignin had all three cellulose vibrations present in its FTIR spectra suggesting that it had considerable cellulose in it. These results are important because they suggest that FA:CC is most effective for extracting lignin from rice husk. FA:CC is probably less effective in lignin extraction from sugarcane bagasse since it was the only biomass among the four that had considerable cellulose vibrations along with lignin vibrations in its spectrum. The extra cellulose content could possibly explain why sugarcane bagasse lignin surpassed coffee chaff in increasing the compressive strength of the cement cylinders. The structure and nature of the biomass apparently have an effect on the quality of lignin extractable with FA:CC.

In the FTIR spectrum of commercially purchased sugarcane bagasse lignin several vibrations are observed. The absorption vibration at 3406.6 cm^{-1} contributed to the -OH broad band of the aliphatic hydroxyl group and phenolic hydroxyl group. The vibration 2934.1 cm^{-1} was contributed to by the C-H band of the methyl group. There was another absorption vibration at 1597.4 cm^{-1} that indicated an aromatic skeletal vibration. There was also a characteristic vibration of 1208 cm^{-1} that indicated aromatic ring breathing with C-H and C=O stretching. Another vibration at 1035.6 cm^{-1} indicates that an aromatic -H out of plane deformation plus a C-O bond in primary alcohols of the guaiacyl type. In the FTIR of CML, there were two vibrations at 1607.3 cm^{-1} and 1413.4 cm^{-1} that indicated the characteristic absorption of the

carboxylate group. These two vibrations showed that carboxyl group was successfully engrafted to the lignin structure (Gan et al., 2013).

Table 3-3: Presence of lignin vibrations in various types of lignin

Lignin from Different Biomass	Lignin Vibration Wavenumber (cm ⁻¹)	Present?	Area (a.u.)
Rice Husk Lignin	858	Yes	466.4
	1515	Yes	6.0
	1600	Yes	378.6
	1718	Yes	97.0
Corn Stove Lignin	858	Yes	65.7
	1515	Yes	1.5
	1600	Yes	13.0
	1718	Yes	7.0
Coffee Chaff Lignin	858	Yes	36.1
	1515	Yes	30.5
	1600	No	
	1718	Yes	19.6
Sugarcane Bagasse Lignin	858	Yes	22.6
	1515	Yes	4.8
	1600	Yes	45.0
	1718	Yes	18.8

Table 3-4: Presence of cellulose vibrations in various types of lignin

Lignin from Different Biomass	Cellulose Vibration Wavenumber (cm ⁻¹)	Present	Area
Rice Husk Lignin	896	No	
	1060	No	
	1162	No	
Corn Stove Lignin	896	No	
	1060	No	
	1162	Yes	9.9
Coffee Chaff Lignin	896	No	
	1060	Yes	35.8
	1162	No	
Sugarcane Bagasse Lignin	896	Yes	10.7
	1060	Yes	10.9
	1162	Yes	44.1

The focus of this discussion has concentrated on the vibrations that are most characteristic of the substances. Other relevant vibrations exist in the spectra that are less important but could be studied further. Future work could include studying these less important vibrations to find out more information on the lignin structures.

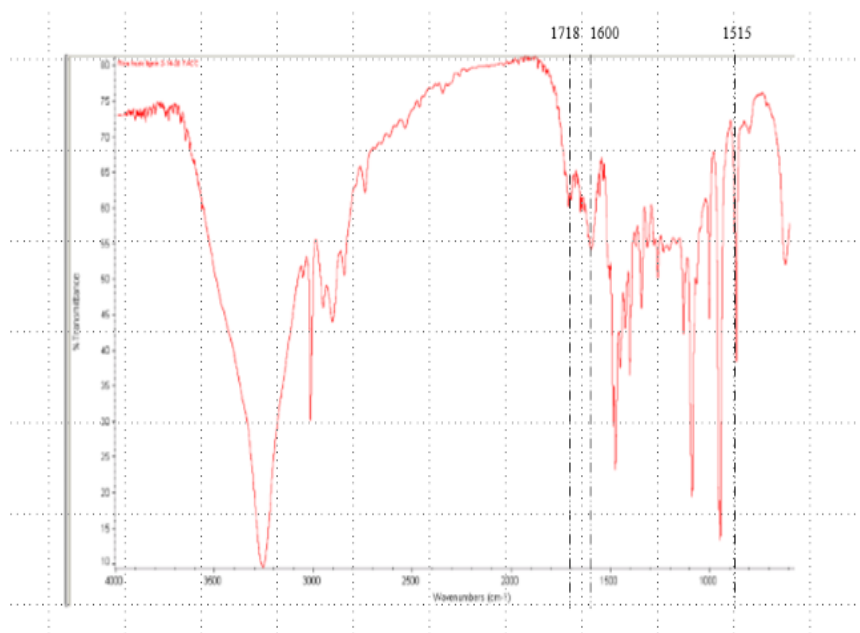


Figure 3-3: FTIR spectra of rice husk lignin

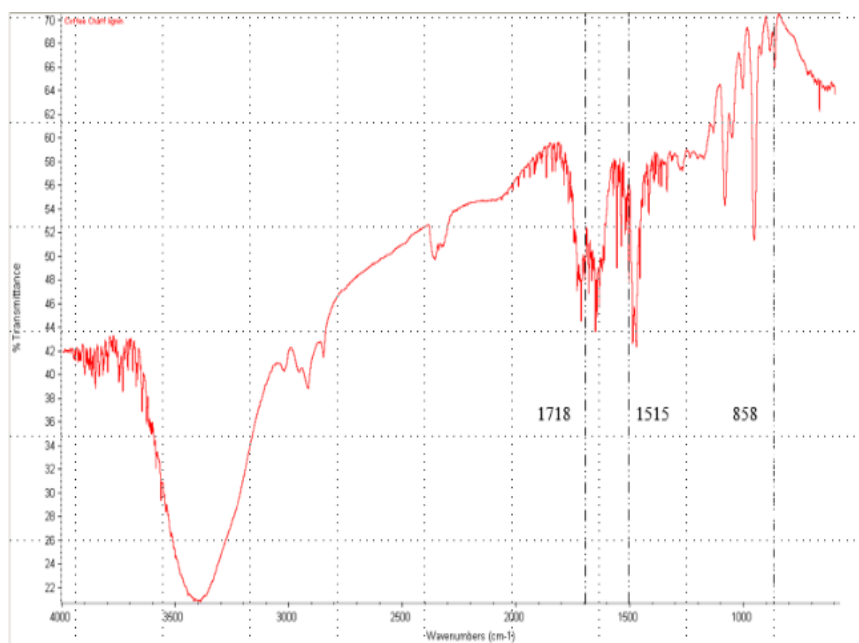


Figure 3-4: FTIR spectra of coffee chaff lignin

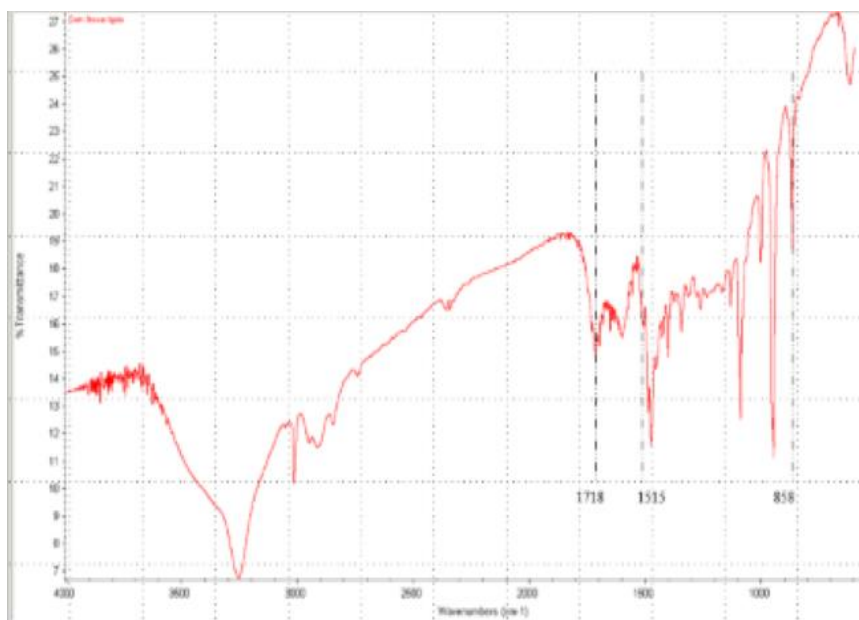


Figure 3-5: FTIR spectra of corn stove lignin

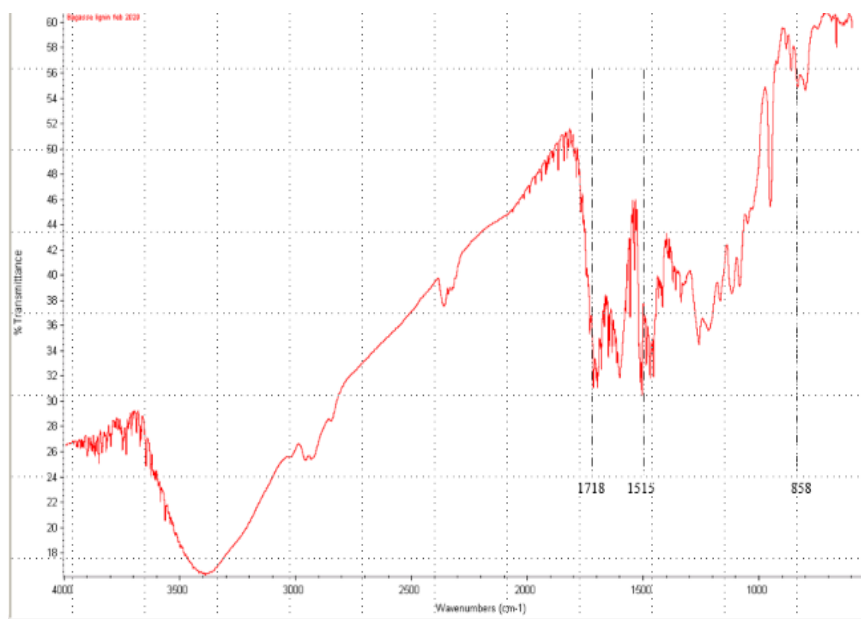


Figure 3-6: FTIR spectra of sugarcane bagasse lignin

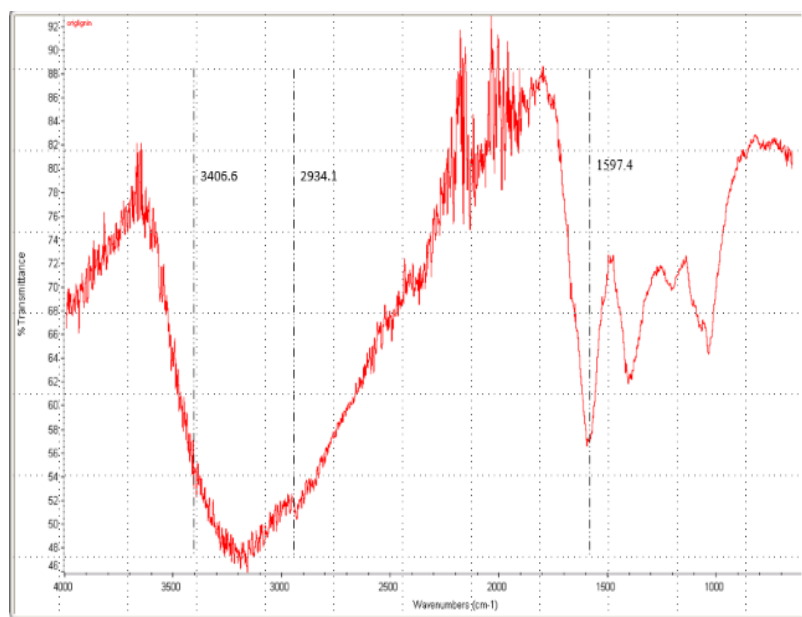


Figure 3-7: FTIR spectra of commercially purchased sugarcane bagasse lignin

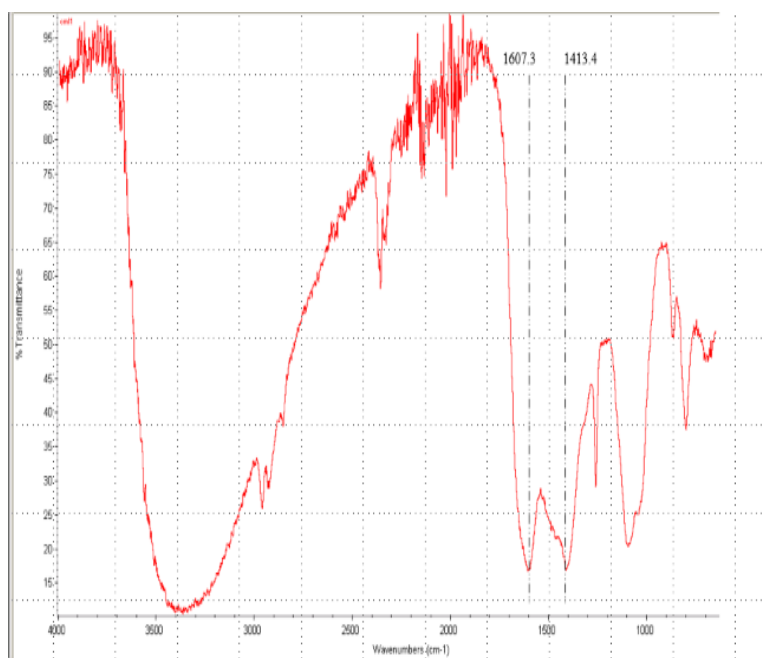


Figure 3-8: FTIR spectra of carboxymethylated sugarcane bagasse lignin

CHAPTER 4

CONCLUSION AND FUTURE WORK

4.1 Conclusion

In the present study, several observations can be made. Pretreatment with the DES FA:CC can successfully extract lignin-rich material from rice husks, corn stover, coffee chaff and sugarcane bagasse. Carboxymethylation of commercial sugarcane bagasse lignin is possible. Lignin extracted from coffee chaff and sugarcane bagasse are feasible plasticizer candidates, since when used as a plasticizer at 0.3 wt% they increased the plasticity of cement paste considerably, as measured by the mini-slump cone test. Since they come from waste biomass, such plasticizers would be more sustainable than some presently used plasticizers sourced from fossil fuels. However, carboxymethylated lignin is not likely to be useful as a plasticizer, since adding it at 2 wt% or 4 wt% reduced the cement's workability as measured by the mini-slump cone test.

Carboxymethylated lignin did not appear to improve compressive strength or porosity. Adding lignin extracted from coffee chaff and sugarcane bagasse at 0.3 wt% significantly increased compressive strength and reduced porosity compared to control, improving the cement's properties. Thus, these two waste biomass have the potential to play a role in improving the sustainability of cement.

4.2 Future Work

Lignin in this work has been extracted using DES FA:CC. Other DES could be used such as lactic acid - ChCl or acetic acid -ChCl. These or other ecofriendly DES could be used on waste biomass to find which DES gives the best yield. Also, in the carboxymethylation process, pH could be varied to see if carboxymethylated products using different pH would impact cement mixtures differently. NMR spectral analysis could be performed on the products to characterize them for deeper understanding. A further in depth analysis of FTIR spectra could be performed. Lignin and its carboxymethylated products could be used as plasticizers in cement mixtures at various concentrations other than those used in this project to optimize the desired properties.

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