Pretreatment of Lignocellulosic Biomass with Acetic Acid, Salts, and Ionic Liquids

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Abstract

As a renewable non-food resource, lignocellulosic biomass has great potential as an energy source or feedstock for further conversion. However, challenges exist in transportation, storage, and use of this perishable resource with relatively low fuel value compared to fossil fuels. Pretreatment of recalcitrant lignocellulosic biomass can facilitate its energy densification compared to the raw biomass. Pretreatment can also fractionate it into its components, which can then be used as platform chemicals for further conversion.

Hydrothermal Carbonization (HTC), also known as wet torrefaction, is a pretreatment where biomass is immersed in liquid water under an inert atmosphere and heated to temperatures between 200 and 300 °C at pressures which ensure that the water remains liquid. HTC’s products include a solid residue (biochar) of increased fuel value and a liquid solution of five carbon and six carbon sugars, along with acetic and other organic acids and furfurals. Additives to the basic process can enhance the higher heating value (HHV) of the biochar. Adding acetic acid and/or Li chloride to the standard HTC process, when applied to loblolly pine at 230 °C, increases the HHV of the biochar up to 30% and removes cellulose from the raw biomass. Adding Ca lactate and Ca chloride to the HTC pretreatment at 260 °C of loblolly pine also enhances the reactions occurring so that the resulting biochar has increased HHV compared to that with no salt added. Ca salts can reduce SOx and NOx emissions from coal thermal conversion processes. If pretreated biomass with a Ca salt adhering to it is co-fired with coal, emissions may be
reduced while less coal is needed. Adding Ca lactate, Li chloride, and Ca chloride to HTC pretreatment also reduces reaction pressure, enhancing process safety.

An alternative to HTC pretreatment is pretreatment of biomass with ionic liquids. Rice hulls, a particularly recalcitrant biomass, are available in vast quantities worldwide. Some ionic liquids, which have very low vapor pressures and are considered “green” solvents, can be used to dissolve biomass. The ionic liquid 1-ethyl-3-methylimidazolium acetate (EMIM Ac) is capable of removing lignin from rice hulls, while ethanol can precipitate lignin out of the used EMIM Ac. The remaining cellulose may be quite available for further conversion to bio-ethanol via enzymatic hydrolysis and fermentation. Additives to the HTC pretreatment process and the use of “green” ionic liquids at low temperatures and pressures show promise in replacing fossil fuel with renewable lignocellulosic biomass.
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<table>
<thead>
<tr>
<th>pH</th>
<th>Ash %</th>
<th>Reaction Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>2.5%</td>
<td>50 bar</td>
</tr>
<tr>
<td>7.5</td>
<td>3.0%</td>
<td>60 bar</td>
</tr>
<tr>
<td>8.0</td>
<td>3.5%</td>
<td>70 bar</td>
</tr>
</tbody>
</table>

Note: Data subject to error and variability.
Chapter 1

Introduction

1.1 Background

Fossil fuels are, by their nature, limited in quantity. With the increasing amounts of fossil fuels demanded by the developing world, it is only a matter of time before the fuels kindly deposited over great lengths of time in the earth’s crust are depleted. Replacement fuels must be found, and solar energy can only be used for some applications. Due to limitations on battery storage, liquid carbon-based fuels will always be necessary for airplanes, cargo ships, long range trucks, and rockets. Renewable fuels which do not contribute to greenhouse gas emissions, which increase global warming, will be required.

Biomass is an excellent alternative energy source for renewable fuels. It converts diffuse solar energy into carbon based feedstocks, while removing CO₂ from the atmosphere. When biomass-based fuel, or biofuel, is thermochemically converted to produce energy, the CO₂ is released to continue the cycle. In addition, biofuels emit smaller amounts of NOₓ and SO₂ compared to fossil fuels. [1] In this respect, biofuels are superior to the fossil fuels presently used.

Lignocellulosic biomass has been used in the past for transportation fuels, especially in steam locomotives and steamboats, where wood was used as a fuel in a firebox to heat pressurized water and steam in a boiler. The steam produced drove the locomotive or steamboat. However, using unpretreated wood caused difficulties, such as incomplete combustion, hazardous spark production, and dangers due to high pressure steam. Such
boilers were also limited to wood as a renewable fuel, as handling difficulties from other lignocellulosic biomass were too severe for the limited technology of the time period.

Improved pretreatments of lignocellulosic biomass are becoming available to permit this renewable resource to be converted to liquid biofuels, suitable for transportation needs. The wide availability and low cost of lignocellulosic biomass in the United States make it an appropriate energy source compared to fossil fuel crude oil, which fluctuates in both accessibility and price.

1.2 Administrative Strategy

In 2010, the United States produced approximately 5500 thousand barrels of oil per day, while consuming 18,800 thousand barrels of oil per day. [2] Thus, the United States’ dependence on foreign oil is obvious. To encourage reliance on domestic renewable fuels, the Energy Independence and Security Act (EISA) of 2007 was passed, to require that over 36 billion gallons of renewable fuels must be produced and used by 2022.[3-5]

For this reason, it has been estimated that more than $3.8 billion dollars of subsidies have been poured into converting corn into ethanol to blend into gasoline. Unfortunately, such ethanol production requires more fossil fuel energy use than the ethanol energy produced. [6] In addition, using food crops to produce energy seems unethical in a world which requires more food resources, not less. Approximately 925 million people in the world do not have enough to eat. [7] Using non-food resources to produce energy seems more moral than producing food and utilizing it for biofuels. Using lignocellulosic biomass, a non-food resource, for biofuels appears to be the right direction to go, in terms
of research and development. The U. S. Department of Energy’s Billion-Ton Update of
August 2011 estimates there will be 200 million dry tons of forest biomass at less than
$80 per dry ton, and 350 million dry tons of agricultural biomass at $60 per dry ton or
less in the year 2012. [8] This billion ton report expects the quantities to increase in the
future and suggests that land resources in the U. S. are capable of producing biomass
sufficient to replace at least 30% of current petroleum use by 2030. [8]

The availability of low-cost, non-food lignocellulosic biomass in the U. S. makes it
an ideal location to study the process of converting it to biofuels. Optimizing
pretreatment of lignocellulosic biomass is the first step to research before development to
a commercial scale can be attempted.

1.3 Lignocellulosic Biomass

Three essential types of non-food foliage are available which can be useful in
producing biofuels. First, crops, including trees, can be specifically grown for energy
production. Secondly, uncultivated or wild plants can be harvested for use as an energy
source. Lastly, lignocellulosic biomass waste materials from agricultural processing can
be used in energy industries.

1.3.1 Lignocellulosic Biomass Crops

Switchgrass is a highly adaptable lignocellulosic biomass native to the U. S. which
can be grown in poor soil, and also has good tolerance to cold, disease, and insects. It has
a higher heating value (HHV) of ~ 19 MJ/kg. [9] Willow plantations have also been
planted as an energy crop, as have poplar and miscanthus, also known as elephant grass.
Except for switchgrass, which can be grown on marginal soil, energy crops in general displace food crops, and so are not beneficial. [13]

1.3.2 Uncultivated Lignocellulosic Biomass

Uncultivated woody lignocellulosic biomass has been collected as firewood for thousands of years. Mixed wood has been used as a heating source, with clear cutting as an efficient method for obtaining this energy resource. When wood has not been available, twisted straw or dung has been used as an energy source, particularly in the prairies of the U. S. Unless performed in a sustainable manner, such use of biomass can endanger biodiversity and cause erosion. [14]

1.3.3 Lignocellulosic Biomass from Agricultural Waste

The U. S. Billion-Ton Update estimates 244 million dry tons of agricultural wastes and residue exist presently at less than $60/dry ton, so there are exciting possibilities for converting these waste materials into biofuels. Corn is used to feed humans, cattle, pigs, and chickens, as well as for ethanol production. However, after harvesting, about half of a corn plant remains as corn stover, primarily consisting of stalk and leaves. The U. S. Billion-Ton Update estimates 200 million dry tons of corn stover are available for use, with additional resources from sorghum, wheat, barley, oats, and rye straws increasing the potential for conversion to biofuels. Sugar cane residues, cotton gin trash, soybean hulls, and rice hulls are considered secondary process wastes which offer further resources. [8] Considering that more than half of the world’s population relies primarily on rice for sustenance [15], and that the rice hull is approximately 20% of the grain,
learning to use rice hulls productively must be considered an essential part of proper stewardship of the earth’s resources.

1.4 Lignocellulosic Biomass Components

The package of lignocellulosic biomass is carefully designed to protect the processes a plant needs to grow and reproduce. It is mainly comprised of cellulose, hemicellulose, lignin, water extractives, and ash. The fraction of each component varies depending on the type of plant. For example, wood contains about 50% cellulose, while grasses contain only 25-35% cellulose. [16]

1.4.1 Lignocellulosic Biomass Matrix

Figure 1.1 shows the chemical structure of a typical lignocellulosic biomass. The plant cell walls are composed of linear, polymerized glucose units connected by β-(1,4)-glycosidic linkages. Typically, 10,000 to 15,000 repeat units form a single cellulose chain. [17] Hydrogen bonding causes these polymer chains to form a strong linear microfibril, which gives the cell wall a rigid structure. Spiraling hemicellulose polymers protect the microfibril and are connected by 3-dimensional lignin molecules. Aqueous solubles, also known as water extractives, surround this structure and ash, typically metal or silicon oxides, permeates it.
1.4.2 Cellulose

Native cellulose is crystalline due to the strong hydrogen bonding between adjacent polymer molecules. Various kinds of pretreatments can disturb these hydrogen bonds and reduce the degree of polymerization (DP), or number of glucose repeat units. Cellulose polymer molecules do not differ in chemical structure, having no side chains, but the proportion of cellulose in a given biomass does vary. The cellulose content in wood varies between 38% to 55% [18], while grasses typically vary between 20-35% cellulose.[19] Switchgrass, an important energy crop, contains approximately 40%
cellulose. [20] Rice hulls contain 36% cellulose. [21] The cellulose content is important because it can be converted to its basic monomer glucose by acid or enzymatic hydrolysis, providing a source of nutrients for yeast conversion to the biofuel ethanol.

### 1.4.3 Hemicelluloses

The polymer chains of hemicelluloses have short branches, are amorphous, and consist of several possible monosaccharide units. Hemicellulose’s lack of crystallinity permits it to be soluble in water and generally more reactive than cellulose. Its degree of polymerization varies from 50-200. Figure 1.2 shows the various pentoses, hexoses, hexuronic acids, and deoxy-hexoses which can comprise a hemicelluloses monomer. [18]

![Figure 1.2 Schematic diagram of hemicelluloses sugar groups](image)

Lignocellulosic biomass varies in its hemicelluloses content. Hardwood contains up to 35% hemicelluloses, with softwood averaging slightly less. Acetylated lactoglucomannans are the main hemicellulose in most softwood species. [22]
Switchgrass has a 29% hemicelluloses content while rice hulls are 12% hemicelluloses. Hemicelluloses, after enzymatic hydrolysis using xylanases, also can be converted into xylose. Xylose-glucose mixtures can be co-fermented using a genetically modified *Saccharomyces* yeast to produce biofuels [25-26]

### 1.4.4 Lignin

Lignin, a cross-linked polymer, has a very complex and non-repeating structure. It is difficult to isolate lignin from lignocellulosic biomass, as it is an essential bonding component of the lignocellulosic matrix. It is covalently bound to hemicelluloses and is hydrophobic, protecting the matrix from water. Figure 1.3 shows a lignin segment.

![Lignin Structure](image)

Figure 1.3 A typical lignin structure. [27]
Lignin in hardwoods contains coniferyl alcohol (also referred to as guaiacyl) and sinapyl alcohol (also called syringyl). [28] Hardwoods have between 18-25% lignin. Softwood lignin is fashioned primarily from coniferyl alcohol and softwoods typically contain 27-38% lignin.[29-30] Grasses, including switchgrass, contain both coniferyl alcohol and sinapyl alcohol, along with small amounts of p-coumaryl alcohol (p-hydroxyphenyl). [31-33] Grasses have ~20% lignin, with switchgrass having a lignin content of ~30%. [33-34] Rice hull lignin has been found to consist mostly of guaiacyl and p-hydroxyphenyl units. [35] Rice hulls contain 15% lignin. [21] The protective presence of lignin in unpretreated lignocellulosic biomass causes difficulties in accessing cellulose to produce biofuels or paper.

1.4.5 Water Extractives

Water extractives are those compounds which are water-soluble in lignocellulosic biomass. They include fats, fatty acids, starches, waxes, terpenes, terpenoids, turpentine, rosin, pitch, and phenolic compounds (stilbenes, lignans, tannins, flavinoids, phenolics, troplones, and coumarins). They comprise approximately 2-5% of woody biomass, but are generally 5-15% of nonwoody biomass. Hardwoods tend to have more extractives than softwood. [36]

1.4.6 Ash

Ash consists of inorganic materials in biomass which are stable when heated to greater than 575 °C in an oxidizing environment. The ash of woody biomass contains calcium carbonate, potassium salts, phosphate, and trace amounts of metals. Woody
biomass contains less than 1% ash. Non-woody biomass, such as switchgrass and rice hulls, contain silica, in addition to the aforementioned. Switchgrass contains about 10% ash, while rice hulls are approximately 20% ash. [37] Rice hull ash has been found to have many uses, including adsorbents, insulation material, and reactants for catalyst production. [38]

1.5 Conversion Routes for Improved Fuels from Biomass

Numerous methods have been used to convert either dry or wet biomass into useful biofuels. Drying biomass prior to further processing reduces its mass, decreasing transportation costs, as well as preventing substantial decomposition. However, energy expenditures for drying can be high. Although biomass can be sun-dried, thus reducing energy costs, such a method is often time-consuming while giving less reproducible results. [39] Using biomass as produced, without drying, can limit the type of processing possible. Determining the optimal process for a particular biofuels process is essential in efficiently solving the global need for renewable energy.

1.5.1 Conversion of Dry Biomass

Several thermochemical conversion processes can use dry biomass. The time-honored method of combustion (also known as incineration) converts biomass directly into flue gases for direct heating or steam generation for electrical power production. However, it also produces CO, SO$_x$, and NO$_x$, as well as fine particulates. A second process, called gasification, reacts biomass with a controlled amount of O$_2$, air, or steam to produce syngas, a mixture of CO and H$_2$. Syngas can be utilized by internal
combustion engines or catalytically converted into liquid fuels. This process is more efficient than combustion, but tar production can be a problem. Biomass pyrolysis is a third method used on dry biomass. It involves thermal decomposition of biomass in the absence of oxygen, and can use a variety of residence times and temperatures. Fast pyrolysis, which uses a high temperature and fast heating rate, can yield bio-crude-oil, a liquid which can be upgraded by hydrotreating to hydrocarbon gasoline [40].

Mechanical or solvent extraction of biomass can produce valuable biofuels. Sawdust, a lignocellulosic biomass already mechanically reduced in size, can be dissolved in ethylene glycol to separate lignin and cellulose-rich fractions. [41] The cellulose separated may then be hydrolyzed enzymatically or using acid to produce glucose for fermentation to ethanol.

1.5.2 Conversion of Wet Biomass

Nearly all biomass is wet (greater than 30% moisture) prior to processing. Several methods exist for upgrading. Supercritical CO₂ can be used to burst algae cells, for example, to release lipids [42] which can be easily converted to biodiesel. Anaerobic digestion can convert biomass to methane rich gas, while enzymatic or acid hydrolysis followed by fermentation can produce ethanol. However, the protective lignocellulosic matrix causes difficulties with these methods. The ammonia fiber explosion (AFEX) process can shatter and split biomass in relatively mild conditions, but requires environmental hazardous chemicals. [43] Supercritical water can be used to extract either pentoses or glucose for fermentation, but requires very high temperatures and pressures, necessitating expensive process equipment. [44] Another method for wet
biomass conversion is hydrothermal carbonization, also known as wet torrefaction.[45] This process uses lower temperatures and pressures, making it less hazardous and allowing for less costly reaction vessels.

1.6 Benefits of Lignocellulosic Biomass Pretreatment

Lignocellulosic biomass is widely available, sustainable, and relatively low cost. [8] However, there are many challenges in utilizing the various forms of lignocellulosic biomass. These challenges can be overcome by pretreatment. Chemical, biological, or thermal pretreatments may be used alone or combined to improve raw biomass materials. [46] Considerations when choosing a pretreatment include chemical cost and environmental safety, energy requirements, time requirements, cost of reactor, and recovery of all components for further use. Any pretreatment should provide for accessibility to valuable biomass components, reduction of decomposition rate, and improvement of transportation and conversion abilities.

1.7 Hydrothermal Carbonization

One promising pretreatment method for converting wet biomass to biofuels is hydrothermal carbonization, also known as wet torrefaction. In this process, biomass, with or without catalyst, is immersed in liquid water and heated to temperatures between 200 and 300 °C at pressures which ensure that the water remains liquid. An inert atmosphere is used. This procedure generates a liquid product which contains pentoses, glucose, and furfurals, as well as organic acids (primarily acetic acid), and a solid lignin-rich product (known as biochar). The biochar has been found to have reduced mass and
increased energy densification. [45,47] The sugars produced have the potential to be fermented to produce ethanol, while the solid lignin-rich product can be pelletized as a fuel for co-combustion with coal for power generation.

1.7.1 Properties of Hot Compressed Water

Water, known as the universal solvent, is useful in dissolving hemicelluloses, especially at temperatures above 180°C. To hydrolyze cellulose, higher temperatures above 200°C and high pressures are necessary. The ionic product of water is maximized at temperatures between 227°C and 327°C [48], so that it may act as an acid or base catalyst for biomass component reactions. In addition, the dielectric constant of water is greatly reduced in this temperature range, compared to ambient temperatures, so that it acts more like a non-polar solvent. [48] Viscosity, density, and heat capacity are also highly sensitive to temperature and pressure changes in this region, permitting reaction rate increases.

1.7.2 Temperature Effects in Hydrothermal Carbonization

Increasing hydrothermal carbonization temperature decreases the mass yield, since more of the biomass components are reacted at a higher temperature, as might be expected considering the Arhenius equation. In addition, energy densification, the ratio of the HHV of pretreated biomass to raw biomass, is increased with higher reaction temperature. [45,47]
1.7.3 Salt Additives

Reports of neutral salts being added to hydrothermal carbonization processes are difficult to find. However, LiCl has been used along with N,N-dimethyacetatamide to disrupt the hydrogen bonding of cellulose which would make it easier to solubilize. [48] Another benefit in adding neutral salts is pressure reduction during hydrothermal carbonization. A third advantage could occur if biochar pellets infused with Ca or Mg salts are co-fired with coal. The presence of Ca and Mg can reduce the amounts of SO$_x$ and NO$_x$ in the flue gases produced. [50-51]

1.7.3 Acid Additives

Many acids have been added to hydrothermal carbonization processes, such as citric acid, acrylic acid and sulfuric acid. [52-55] These acids, when added at the proper level, can catalyze the hydrothermal carbonization reaction. Organic acids, such as acetic acid, formic acid, and lactic acid, are formed during the reaction, and serve to naturally reduce the pH, thus spurring on the reaction.

1.8 Ionic Liquids

Concerns about the ubiquitous use of hazardous volatile organic compounds (VOCs) have encouraged the development of more “green” solvents. Ionic liquids, with their extremely low volatility, have become an exciting new class of solvents for use in separations and reactions. Ionic liquids have been found to have uses in dealing with lignocellulosic biomass. [56]
1.8.1 Properties of Ionic Liquids

Ionic liquids (ILs) are salts with melting temperatures less than 100 °C. The poor coordination between their large cations and their anions of varying size causes them to be liquid at temperatures much lower than typical salts. Since there are many large cations possible, as well as many anions, the possibilities for different kinds of ionic liquids are nearly limitless. Many ILs have been found to dissolve cellulose and/or lignin. [56] Generally, such useful ILs have melting points greater than -70°C and less than 100°C. Rather than having vaporization points, these ILs decompose, usually between 200°C and 300°C. High viscosity can be a challenge in using ILs, as their viscosity can vary between 0.09 Pa-s to greater than 0.3 Pa-s. IL densities are similar to that of water.

1.8.2 Mechanism of Ionic Liquid Interaction with Biomass Components

Hydrogen bonding between adjacent cellulose polymer chains maintains the crystalline structure of the biomass component. Such hydrogen bonding can be disrupted by anions in ionic liquids. The Cl¯ anion in an IL can bond with a cellulose hydroxyl proton, as determined by NMR investigation. [57] Other anions likely perform hydrogen bond disruption in a similar fashion. How ILs solubilize lignin is not thoroughly investigated yet. Cellulose dissolved in an IL can be reconstituted by the addition of water to form a hydrodynamic shell around the IL’s ions, allowing the intra and intermolecular hydrogen bonds of the cellulose to re-form. [58]

1.8.3 Temperature Effects on Ionic Liquids
The most important temperature effect on ILs is the fact that increasing temperature decreases viscosity. [59] A lower viscosity permits filtering, stirring, or other handling of an IL. However, use of ILs is limited to temperatures lower than the decomposition temperature.

1.9 Project Objectives

The objective of this thesis is to understand the effects of two types of pretreatment on biomass. First, the effects of additives on hydrothermal carbonization of loblolly pine are investigated. Particular attention is paid to mass reduction, energy densification, and process pressure reduction when acetic acid, Ca and Mg salts, and LiCl are added to the hydrothermal carbonization pretreatment process. The large effect of LiCl addition on the energy densification of loblolly pine suggests that Cl\(^-\) ions do have an unusual ability to disrupt cellulose hydrogen bonding. While the solubility of LiCl in water is limited, ionic liquids, used alone as a pure material, may be used to pretreat lignocellulosic biomass at higher ion concentrations. A waste material, rice hulls, can be pretreated with various ionic liquids to investigate their ability to deconstruct a lignocellulosic biomass into its components. This new approach to pretreatment may prove valuable in the struggle to produce biofuels from biomass.

1.10 Organization of Thesis

Chapter 2 shows the effect of additives to the hydrothermal carbonization process on pretreated biomass properties such as mass yield, energy densification, and biomass component change. Adding acetic acid or LiCl, as well as a combination of the two, is
investigated and discussed. Loblolly pine is used as a representative biomass in this study. Most of the content of this chapter has already been published in by Lynam et al. in 2011. [60]

Chapter 3 shows the effects of Ca and Mg salts, when used in hydrothermal carbonization, on pretreated biomass properties. In addition, the effect of these salts on reaction pressure is emphasized. Loblolly pine is again used for the biomass, so that comparisons can be made with the previous additive investigation. Chapter 3 is in preparation for publication, and is formatted accordingly.

A new pretreatment method, low temperature dissolution of biomass in IL, is investigated in Chapter 4. Rice hulls, a widely available secondary agricultural waste, are used in this study. Temperature and reaction duration are varied to determine optimal conditions for dissolution of this highly recalcitrant biomass. The effects on biomass component removal are determined as a function of dissolution conditions for four different ILs. Chapter 4 has been submitted for publication and is formatted accordingly.

Chapter 5 summarizes the conclusions of the previous chapters and discusses recommendations for future research.
1.11 References


Chapter 2

Acetic Acid and Lithium Chloride Effects on Hydrothermal Carbonization of Lignocellulosic Biomass

As a renewable non-food resource, lignocellulosic biomass has great potential as an energy source or feedstock for further conversion. However, problems exist with transportation and storage of this geographically scattered and perishable resource. Hydrothermal carbonization treats any kind of biomass in 200 to 260°C compressed water under an inert atmosphere to produce a hydrophobic solid of reduced mass and increased fuel value. A maximum in higher heating value (HHV) was found when 0.4 g of acetic acid was added per g of biomass. If 1 g of LiCl and 0.4 g acetic acid were added per g of biomass to the initial reaction solution, a 30% increase in HHV was found compared to the pretreatment with no additives, along with greater mass reduction. LiCl addition also reduces reaction pressure. Addition of acetic acid and/or LiCl to hydrothermal carbonization each contribute to increased HHV and reduced mass yield of the solid product.

2.1. Introduction

Energy independence has been a goal in the United States since the oil crisis in the 1970’s. Interest in “homegrown” fuels has fluctuated directly with the price of imported non-renewable fuels. However, using potential food, such as corn, to produce energy seems unethical in a world of limited caloric resources. As a non-food renewable resource, lignocellulosic biomass could be used as an important starting point to produce biofuels indefinitely. Enhanced biofuels can be produced from low-value biomass via two methods. With biochemical conversion, biomass is broken down by enzymatic or
chemical processes and then converted to ethanol through fermentation. In thermochemical conversion, biomass is broken down to intermediates using heat and upgraded to fuels using both heat and pressure with catalysts present. However, lignocellulosic biomass exists in many diverse forms. Crops such as hard or soft woods, switch grass, or miscanthus can be grown, while waste products from food production, such as rice hulls, corn stover, straws, and bagasse, can be obtained easily and cheaply. The great variation in solids handling for these different feedstocks causes difficulties in further processing. Also, the seasonal nature of these plant-based materials requires good storage properties. Pretreating biomass by heating it in an inert environment can improve the usefulness of these feedstocks (Prins et al., 2006a, 2006b; Yu et al., 2008).

Pretreatment can be performed as a dry process or as a wet process. The dry process is called dry torrefaction or mild pyrolysis. When done in hot compressed water, the process is often referred to as wet torrefaction, biomass hydrolysis, or hydrothermal carbonization. Relatively simple processes, both pretreatments increase not only a biomass’s density to decrease transportation costs, but also its hydrophobic behavior for simpler storage. Torrefaction’s solid product is easily crushable, regardless of the particular initial feedstock, leading to a more uniform feed for processing. In addition, the process improves the solid product’s heating value on a weight basis, with increased carbon percentage, making it more suitable for co-firing in coal power plants. Although pretreatment produces some carbon dioxide, carbon is taken from the atmosphere and fixed in the original biomass, so the process is carbon neutral.

Dry torrefaction typically is performed between 225 and 300 °C with reaction times of between 30 min and several hours (Prins et al., 2006a, 2006b; Sadaki and Negi, 2009).
Hydrothermal carbonization or wet torrefaction is run at slightly lower temperatures (180 to 260 °C), with liquid water used, necessitating high pressures of up to 4.6 MPa gauge. The reactions involved do not proceed significantly at temperatures lower than 180 °C. Although reaction time for hydrothermal carbonization can be several hours, the initial 20 minutes appear to generate the vast majority of product (Knezevic et al., 2010).

Hydrothermal carbonization is preferred for several reasons. At temperatures of 227 °C to 327 °C, the ionic product of water is maximized, leading to the possibility that it could act as an acid or base catalyst for reactions. Also, the dielectric constant of water is much lower at these temperatures than ambient temperatures, causing it to behave more like a non-polar solvent (Yu et al., 2008). Hydrothermal carbonization when used at similar temperatures to dry torrefaction is more effective in providing energy densification by lowering mass and increasing higher heating value (HHV) (Yan et al., 2009). The characteristics of hydrothermal carbonization, including the shorter reaction time at lower temperature and reduced equilibrium moisture content, which reduces degradation over time, indicate its greater feasibility for a seasonal feedstock (Yan et al., 2009).

Using hydrothermal carbonization, the energy densification ratio, the ratio of the heating value of the pretreated solid fuel product to that of the original biomass, can be increased by 3 to 47%, depending on the type of biomass and reaction conditions. Reaction temperature has been found to be the most significant variable in changing the solid product qualities, with higher temperatures decreasing mass yield and increasing HHV. Biomass pretreated by hydrothermal carbonization has increased fixed carbon and atomic carbon, implying it has become a fuel similar to low rank coal. In addition,
reduced equilibrium moisture content in pretreated biomass indicates a more hydrophobic nature leading to better storage properties (Acharjee, 2010).

Hydrothermal carbonization produces not only a solid fuel for use or subsequent conversion, but also other potential high-value products. Glucose, among other simple sugars, and 5-hydroxymethyl furfural (5-HMF) can be precipitated in significant quantities from the aqueous product stream. The aqueous stream also contains volatile acids. For example, when loblolly pine was pretreated at 230 °C for 5 minutes, 0.025 g of acetic acid was produced per gram of original wood. Formic acid (0.0085 g) and lactic acid (0.0026 g) were produced as well (Yan et al., 2010). These acids lower the pH in the reaction system as they are produced.

The role of pH in hydrothermal carbonization has not been fully explored. The reaction rate at 300 °C for solutions of glucose, which can serve as a model for biomass, was observed at pH levels of 1 to 14, but no clear trends emerged (Knezevic et al., 2009). An initial pH of greater than 7 leads to a liquid rather than solid product (Ando et al., 2000; Hu et al., 2008). Many hydrothermal carbonization processes report the addition of such acids as citric acid (Hu et al., 2008; Titirici and Antonietti, 2007), acrylic acid (Demir-Carkan, 2009), and sulfuric acid (X.B. Lu et al., 2009). The effect of acetic acid was chosen for investigation because it is the primary acid produced in hydrothermal carbonization (Yan et al., 2010), thus reducing the complexity of the reaction system. Also, acetic acid could be recycled to treat fresh batches of biomass, minimizing cost. A reaction temperature of 230 °C may be preferable because the degradation of glucose, a valuable product of hydrothermal carbonization, rapidly increases above 230 °C (Yu et
al., 2008). In addition, higher temperatures increase the pressure necessary to maintain liquid water, requiring sturdier reactor walls and making the process more hazardous and expensive. It could be expected that adding lithium chloride would reduce pressure in aqueous systems, as well as having a possible catalytic effect and increasing the activity of the \([\text{H}^+\]) ions in the system, reducing pH. Thus, investigating the effects of both acetic acid and lithium chloride on the hydrothermal carbonization process at 230 °C was deemed useful.

### 2.2. Material and Methods

#### 2.2.1 Biomass

As a typical lignocellulosic biomass, loblolly pine was acquired from Alabama, USA. On a mass basis, it consists of 11.9 % hemicelluloses, 54.0 % cellulose, 25 % lignin, 8.7% extractives and 0.4% ash (Yan et al., 2010). Pine samples were milled to the desired particle size of 14-28 mesh (1.168 to 0.589 mm in diameter) before hydrothermal carbonization. Before treatment, the moisture content was measured to be 5.2 % by weighing a sample, then measuring weight loss after drying for 24 h at 105 °C.

#### 2.2.2 Acetic acid

Glacial acetic acid (Sigma-Aldrich, 99.7+%, ACS Reagent) was diluted with deionized water to 0.64 M acetic acid, 1.24 M acetic acid, 1.79 M acetic acid, and 2.31 M acetic acid. The solutions had pH values of 2.48, 2.31, 2.25, and 2.17.
2.2.3 Lithium chloride

Lithium chloride (Alfa Aesar, anhydrous, 99% min, -20 mesh) was dissolved by stirring into deionized water resulting in either a 4.40 M or a 7.95 M LiCl solution. Thus, either 1 or 2 g of LiCl was added per g of pine for a reaction. For the runs where both LiCl and acetic acid were present, LiCl was stirred into the 1.24 M acetic acid solution so that 1 g of LiCl was added per g of pine. Lithium chloride is extremely soluble in water. The solubility is 0.8 g LiCl/g water at 22 °C, and 1.7 g LiCl/g water at 230 °C (Monnin et al., 2002). Since the Parr reactor used did not have a stirrer, a uniform solution could not be guaranteed, unless the LiCl was able to be dissolved at room temperature. Using 2 g LiCl per g of pine was about half of the solubility limit at 22 °C.

2.2.4 Hydrothermal carbonization

Hydrothermal carbonization of loblolly pine was performed in a Parr Series 4560 bench-top reactor of volume 100 mL (Moline, IL). For each run, loblolly pine was placed in the reactor and either deionized water (as the control), an acetic acid solution, a LiCl solution, or the combination solution was poured in the reactor to cover the biomass. In all runs, water to loblolly pine mass ratio was 5:1. A glass liner was placed in the reactor for the LiCl runs to protect reactor walls from pitting. Acetic acid to loblolly pine mass ratio was varied as 0 g, 0.2 g, 0.4 g, 0.6 g, and 0.8 g of acetic acid to 1 g of loblolly pine. Lithium chloride to loblolly pine mass ratio was either 1 or 2 g of LiCl to 1 g of pine. For the combination run, 1 g LiCl and 0.4 g acetic acid were added per 1 g of pine. After the reactants were loaded, the reactor was purged with nitrogen for 10 minutes to remove oxygen. Heating time from room temperature to 180°C required about 20
minutes, while 4 more minutes were required to heat the reactor to 200°C. In all, reactor
temperature remained above 180°C for 19 minutes or above 200°C for 15 minutes. The
glass liner did not significantly affect the heating rate. Reaction time was 5 minutes after
the set point of 230 °C was reached, after which the reactor was rapidly cooled by
immersion in an ice bath. After immersion, the internal reactor temperature cooled to
below 180°C in less than 1 minute at a rate of approximately 2 K/s and subsequently
cooled to room temperature. The temperature of the reactor was held at 230°C using a
PID controller. Adaptive control was necessary to maintain temperature at 230°C in runs
with LiCl. The reactor pressure was not controlled. For the runs without LiCl, pressure
corresponded to the saturated vapor pressure. Each experiment at the different acetic acid
and LiCl levels was performed at least three times.

2.2.5 Quantitative measurement of reaction products

After cooling the reactor to 25 °C, the gas product was released without further
evaluation. The liquid portion and the hydrothermally carbonized solid were separated by
vacuum filtration using a Buchner funnel with Whatman filter paper (Grade 3, 0.6 µm).
In the experiments with acetic acid, 1.9 g washing water per g loblolly pine was added for
enhanced recovery from the reactor. If LiCl was added, 14.3 g washing water per g
loblolly pine was added to ensure that the LiCl was removed from the solid product. The
hydrothermally carbonized solid was dried at 105 °C for 24 h.
2.2.6 Analyses

The pH of the liquid portion was measured using a digital probe. Differences in pH among runs with the same reaction conditions were ± 0.02 for acetic acid experiments, but as high as ± 0.05 for experiments involving LiCl, probably due to acid error, a time dependent phenomena (McCarty and Vitz, 2006).

Ash analysis in triplicate was performed on all solid samples in which LiCl was added to the reactants. After drying for 24 h at 105 °C, 1 g of the pretreated solid was heated to 575 °C in a muffle furnace and maintained at that temperature for at least 12 h to ensure that only ash remained. Samples were cooled to room temperature in a desiccator before being re-weighed to determine ash percentage (Ehrman, 1994). For the acetic acid only 230 °C treatments of loblolly pine, ash was considered to be 0.4% (Yan et al., 2009).

Heats of combustion (HHV) for both raw loblolly pine and pretreated solid product were measured in a Parr 1241 adiabatic oxygen bomb calorimeter fitted with continuous temperature recording. Samples (0.2 g) were dried at 105 °C for 24 h prior to analysis. HHV values were adjusted to give values on a dry basis for raw loblolly pine.

For solid samples, fiber analysis was carried out using a modified Van Soest method using the ANKOM A200 Filter Bag Technique (Goering and Van Soest, 1970). Solid product samples (0.5 g) of approximately 0.589 mm in diameter were dried at 105 °C for 24 h. After placement in sealed filter bags, samples were digested with neutral detergent to determine neutral detergent fiber (NDF). Digestion with 1 N sulfuric acid detergent determined acid detergent fiber (ADF), and subsequent digestion in 72 % sulfuric acid
gave a value for acid detergent lignin (ADL). The weight percentage extracted by neutral detergent (NDF) is called water extractible. The difference of the NDF and ADF percentage yields the percentage of hemicelluloses, while ADF – ADL gives the percentage of cellulose. The weight remaining after the ADL procedure is considered to be lignin plus ash. Error in component percentages for samples without LiCl is approximately ± 0.5%. If LiCl is added, error is probably an order of magnitude greater, due to interaction of LiCl with the digesting solutions.

High performance liquid chromatography (HPLC) was performed on the liquid product of hydrothermal carbonizations at each acetic acid level. The HPLC system (SHIMADZU, CA, USA) consisted of a system controller (SCL-10A), a liquid pump (LC-10AD), a refractive index detector (RID-6A), an auto-injector (SIL-10AD), and a column oven (CTO-10A). The HPLC system was controlled by a computer running SHIMADZU EZStart software.

Operating conditions were as follows: the chromatographic separation was performed on a BIO-RAD HPLC organic acid analysis column (Aminex® HPX-87H Ion Extrusion Column, 300mm × 7.8mm). The column oven temperature was set at 65 °C. The mobile phase consisted of ultra-pure water containing 0.005 mol·L⁻¹ sulfuric acid. The flow rate of the mobile phase was set at 0.6 mL·min⁻¹ and the injection volume of the auto-sampler was 50 μL.

Identification of organic acids (acetic acid, formic acid, and lactic acid) was made by comparison of their retention times with those of pure standard solutions. Quantification was performed on the basis of linear calibration plots of peak area against concentrations.
Calibration lines were constructed based on five concentration levels of standard solutions. Dilution of samples was necessary if the concentrations of organic acids were out of the range of concentrations shown on calibration lines.

2.3. Results and discussion

2.3.1 Lithium chloride effect on reaction pressure

Pressure of the standard reaction with no additives is approximately 4.6 MPa gauge at 260 °C, and 2.6 MPa gauge at 230 °C. These pressures correspond to the vapor pressure of water, and are largely unaffected by the presence of biomass. With the addition of 1 g of LiCl per g pine, gauge pressure at 230 °C is reduced to 1.8 MPa, while 2 g of LiCl per g pine reduces the reaction gauge pressure to 1.2 MPa. Zeng et al. (2006) describe the vapor pressure of aqueous LiCl at high temperatures, which is substantially reduced compared to pure water. Lowering the pressure of the process improves the safety of the operation, and allows for the use of less expensive reactor vessels, with decreased capital costs.

2.3.2 Mass yield variation with acetic acid and lithium chloride levels

Mass yield is defined as the mass ratio of dried pretreated solid to dried biomass. Figure 2.1 shows the effect of acetic acid level on mass yield. Although adjacent levels may not be statistically different, the downward trend is clear. The addition of greater amounts of acetic acid results in decreased mass yield. As discussed below, more cellulose has been reacted, indicating a greater extent of reaction with the addition of higher acetic acid levels. Acetic acid has been suggested to perform a catalytic role in
hydrothermal carbonization (Xu and Thomsen, 2009). When fructose is used as a model compound for biomass and hydrothermal carbonization at 220 °C is performed, a higher rate of decomposition of fructose is achieved with an acetic acid addition of 0.05 g per g fructose, suggesting that activation energy was decreased (Li et al., 2009). Higher levels of acetic acid addition likely increase severity of reaction, similar to a temperature increase. Increasing reaction temperature has been shown to decrease mass yield. For loblolly pine, at a reaction temperature of 200 °C, mass yield is 88.7%, decreasing to 70.6% at 230 °C, and 57.0% at 260 °C (Yan et al., 2009).
Figure 2.1 Effect of acetic acid and lithium chloride addition in hydrothermal pretreatment on mass yield of solid product
When an aqueous solution of LiCl is used in hydrothermal carbonization, greatly reduced mass yield results (Figure 2.1). Lithium chloride has been used in combination with N,N-dimethyacetatamide to decrease the crystallinity of cellulose by disrupting the strong, water-mediated H-bonding of the polymer chains (Marson and El Seoud, 1999). The cellulose crystal has been shown to change structure from cellulose I to cellulose II, a less crystalline form, in hot compressed water treatment at temperatures over 200 °C and to decompose completely above 300 °C (Kobayashi et al., 2009). Lithium chloride likely performs a catalytic role in the process (Kawamoto et al., 2008), lowering the activation energy necessary for structure change and decomposition of cellulose. Looking at fiber analysis data indicates that the percentage of cellulose, typically 54.0% for loblolly pine (Yan et al, 2009), is greatly reduced when LiCl is added to the process compared to the control (Figure 2.2). Increasing the level from 1 to 2 g LiCl per g pine does not cause further mass yield decreases. When both acetic acid and LiCl are added to the initial reaction solution, mass yield is reduced still further (Figure 2.1). At 230 °C, a combination of acetic acid and LiCl produces a mass yield even lower on average than that produced at a reaction temperature of 260 °C. Obviously, an additive effect from the two components exists which decreases the mass yield. Adding LiCl to acetic acid reduces pH, indicating that the activity of the acetic acid has been enhanced. This effect may partially explain the greatly reduced mass yield.
Figure 2.2 Effect of LiCl addition in hydrothermal pretreatment on cellulose and lignin content in solid product

When certain substances are added to water the dielectric constant decreases, making the pretreatment solvent more effective for non-polar substances. For example, at 25 °C, the dielectric constant of water is 78.46 (Uematsu and Franke, 1980). For a mixture of water with 0.045 mole fraction acetic acid, a slightly lower level than that used in the 0.8 g acetic acid per g biomass experiments, the dielectric constant is 73.2 (Kaatze et al., 1991). Adding LiCl to water also decreases the dielectric constant. In aqueous LiCl solutions with concentrations greater than 4 M, the dielectric constant would be expected to be lower than 50 (Kalcher and Dzubiella, 2009). This large and probably additive effect on dielectric constant may increase the extent of reaction.
2.3.3 Higher heating value variation with acetic acid and lithium chloride levels

Figure 2.3 shows the effect of acetic acid level on heat of combustion. The average HHV of raw loblolly pine is 19.9 MJ/kg. The addition of acetic acid at any level increases the HHV of pretreated biomass. A maximum in HHV is found at the 0.4 g acetic acid added per g loblolly pine level. A significant increase in HHV results from adding 1 g of LiCl per g pine, with a slight possible further increase when 2 g of LiCl per g pine is added (Figure 2.3). Again, an additive increase in HHV is noted when 0.4 g acetic acid per g pine is added combined with 1 g of LiCl per g pine, with HHV 30% higher than that of a run with no additives. The HHV of the combination at 230 °C is the same as that at 260 °C with no additives. Therefore, the same solid fuel could be produced at lower temperature and pressure, reducing costs of the process and improving safety. However, a glass lining for the reactor would be required because the chloride ion in LiCl could cause pitting. To combine the effect of both lithium and acetic acid addition without adding chloride ions, it is possible that lithium acetate could be useful in the process.
Figure 2.3 Effect of acetic acid and lithium chloride addition in hydrothermal pretreatment on higher heating value (HHV) of solid product. The HHV of untreated loblolly pine is 19.9 MJ/kg.
To explain this higher heating value data, the changes in biomass composition produced by the hydrothermal carbonization process must be examined. Biomass consists of 5 main components: hemicelluloses (pentosans), cellulose, lignin, aqueous solubles, and ash. Loblolly pine in particular has been measured by fiber analysis to have 11.9% hemicelluloses, 54.0% cellulose, 25.0% lignin, 8.7% aqueous soluble, and 0.4% ash (Yan et al, 2009). At 230 °C in any hydrothermal carbonization reaction, the hemicelluloses are to a great extent solubilized (Yan et al., 2009; Yan et al, 2010). Figure 2.4 shows the variation of the percentages of cellulose, lignin, and aqueous solubles when different levels of acetic acid are added. Increasing reaction temperature has been shown to progressively remove more cellulose from the solid product, as well as to increase HHV. For example, for loblolly pine, at a reaction temperature of 200 °C, the percentage of cellulose has been measured to be 47.4%, decreasing to 44.1% at 230 °C, and 33.9% at 260 °C. In the same study, HHV is increased from 21.12 MJ/kg at 200 °C to 22.09 MJ/kg at 230 °C to 26.55 MJ/kg at 260 °C (Yan et al., 2009). Removal of cellulose appears to correlate with increased HHV. The 0.4 g added acetic acid per g pine level has the lowest cellulose percent indicating that the highest possible HHV might be expected (Figure 2.4).
Figure 2.4 Effect of acetic acid addition in hydrothermal pretreatment on fiber analysis of solid product
With increasing reaction temperature, higher percentages of lignin and aqueous solubles were found from fiber analysis, suggesting that higher percentages of these components may increase HHV (Yan et al., 2009). Looking at Figure 2.4, lignin percentages appear to be fairly constant, although the 0.2 and 0.4 g added acetic acid per g pine may be slightly higher. Both cellulose and hemicelluloses are reported to have a HHV of 17.58 MJ/kg, and lignin’s HHV is 23.32 to 26.63 MJ/kg (Demirbas, 2005). Increasing acetic acid levels cause more cellulose to be reacted, possibly increasing the HHV of the solid product because a greater proportion of lignin remains. However, since the changes in lignin content are small (Figure 2.4), investigating differences in aqueous solubles is appropriate. Aqueous solubles are considered to be liquid product precipitating onto the pores of the solid product (Yan et al., 2009). At a 230 °C reaction temperature, the composition of the liquid product’s precipitate has been determined to be primarily 5-hydroxymethyl furfural (5-HMF) and glucose. Production of HMF has been shown to increase with increasing levels of acetic acid addition to raw corn stover under hydrothermal pretreatment at 195 °C (Xu and Thomsen, 2010). If acetic acid addition causes more 5-HMF to be formed compared to glucose, more 5-HMF than glucose likely remains precipitated in the solid product’s pores. The HHV of 5-HMF can be calculated from its heat of formation to be 22.06 MJ/kg (Verevkin et al., 2009), while the HHV of glucose is 15.57 MJ/kg. Thus, a greater HHV may be linked to increased 5-HMF content in and a higher percentage of the aqueous solubles. However, too high an acid level may encourage decomposition of 5-HMF to levulinic acid or formic acid, lowering the HHV (Girisuta et al., 2006).
Hemicelluloses are almost completely hydrolyzed at 200 °C in any hydrothermal carbonization reaction (Yan et al., 2009; Yan et al., 2010). Slightly more hemicellulose remains when acetic acid is added to the pretreatment process (Figure 2.4). The data for 0.8 g acetic acid added per g loblolly pine show only slightly lower lignin and aqueous solubles percentages compared to the 0.4 g level, but a noticeably lower hemicellulose percentage (Figure 2.4). Since hemicellulose has a higher HHV than the sugars to which it converts, this may account partially for the lower HHV that the 0.8 g acetic acid added per g loblolly pine level displays.

Figure 2.2 shows the percentages of cellulose and lignin in the solid samples with LiCl added to the reaction solution. The percentage of cellulose in the solid product decreases substantially with LiCl addition while the percentage of lignin simultaneously increases. When a mass balance is performed on lignin, for the 2 g LiCl per g pine and the combination 0.4 g acetic acid and 1 g LiCl per g pine runs, lignin appears to be generated. In reality, lignin-like substances not dissolvable by digestion in 72 % sulfuric acid are generated. Hawamoto et al. (2008) reported that LiCl has a catalytic action on the polymerization of levoglucosan. As discussed earlier in this section, lignin has a much greater HHV than cellulose and removal of cellulose is linked to higher HHV. In addition, aqueous solubles were about twice as high for runs with LiCl added compared to those with no additives. These facts likely account for the greatly increased HHV in the products with LiCl addition.

When both 1 g of LiCl and 0.4 g of acetic acid are added per g of pine, the percentage of lignin is about twice that of a standard pretreatment run with no additives (Figure 2.2),
which at least partially explains the large increase in HHV. With both additives, cellulose structure, as described in section 3.2, must be so greatly disrupted that cellulose can be removed from the solid product by digestion with 1 N sulfuric acid detergent, which normally only removes hemicellulose. Otherwise, in this case, a negative value for cellulose percentage would be calculated, which is a physical impossibility, while a hemicellulose value higher than that of raw loblolly pine would be indicated. Since for the control runs with no additives and for the runs with LiCl added, hemicellulose is completely removed from the solid product, cellulose probably should be calculated in this case as NDF – ADL, rather than ADF – ADL, as discussed in section 2.6. Thus, the cellulose percentage for 1 g of LiCl and 0.4 g of acetic acid added per g of pine would be 8%, an extremely low value. Acetic acid and LiCl apparently interact to cause increased conversion of cellulose in the process. While higher heating value and mass reduction of hydrothermal carbonization’s solid product are emphasized in this study, higher levels of conversion of cellulose to glucose in the liquid product may be helpful in further conversion by fermentation to bioethanol. Alternatively, if the glucose further reacts to form 5-HMF, 5-HMF may be converted to 2,5-dimethylfuran, a biofuel with an energy density greater than that of ethanol.

2.3.4 Energy densification and energy yield change with acetic acid and lithium chloride levels

Energy densification ratio is defined as the ratio of the HHV of dried pretreated solid to the HHV of dried biomass. The HHV of dried untreated loblolly pine was measured to
be 19.9 MJ/kg. The energy densification ratio at a reaction temperature of 230 °C varied from 1.06 with no acetic acid addition to a maximum of 1.12 for 0.4 g acetic acid added per g loblolly pine. The addition of lithium chloride resulted in an energy densification ratio of 1.22 for 1g and 1.28 for 2 g LiCl per g pine. Adding both 0.4 g acetic acid and 1 g LiCl per g pine gave an energy densification ratio of 1.34, increasing the heating value of the solid fuel by 34% compared to the original biomass.

The energy yield is defined as the mass yield times the energy densification ratio and indicates the total fuel value of the product solid relative to the fuel value of the original biomass. Figure 2.5 shows the energy yields at the different reaction conditions. As determined by single factor (one way) ANOVA analysis, there was no statistical difference at a 95% confidence level among energy yields with or without additives, except when 0.8 g of acetic acid or 2 g LiCl per g pine was added. When 0.8 g of acetic acid per g pine was added, energy yield was decreased (p < 0.05). Mass yield in this case was lower than that without additives, and HHV was similar, causing a lower energy yield (Figure 2.1 and Figure 2.3). For the 2 g LiCl per g pine runs energy yield was higher (p< 0.05), due to the slight decrease in mass yield and the substantial increase in HHV compared to those for the runs with no additives (Figure 2.1 and Figure 2.3). For all the other cases, including the one where both 0.4 g of acetic acid and 1 g LiCl per g pine was added, energy yield was the same at 0.8. Of the original energy contained in the raw biomass, 80% remained in the pretreated solid product. Even though mass yield was decreased with increasing acetic acid addition and with the addition of lithium chloride, due to increased energy densification ratio, the energy yield stayed high. Adding acetic
acid and/or lithium chloride does no harm to energy yield, unless levels higher than 0.6 g acetic acid per g pine are used.
Figure 2.5 Effect of acetic acid and LiCl addition in hydrothermal pretreatment on energy yield (product of mass yield & energy densification) of solid product
2.3.5  Final pH change and concentration change with acetic acid and LiCl addition

Figure 2.6 shows the pH values of the liquid product of the hydrothermal carbonization process when varying amounts of acetic acid were added. These values were measured after 1.9 g of washing water per g loblolly pine was added to the final product. As expected, addition of more acetic acid reduces the pH, causing more severe reaction conditions. When no acetic acid is added to the initial reactants, 0.03 g of acetic acid is produced per g original pine (Yan et al., 2010). This quantity, diluted in 5 g initial water plus 1.9 g washing water, should result in a solution with the calculated pH of 2.95. This concurs with the measured value. However, if 0.4 g acetic acid is added to the 0.03 g acetic acid expected to be produced, with the same amounts of water added, a pH of 2.39 would be expected. This expected value is significantly lower than the measured value of 2.61. Similar results are found for all levels of addition of acetic acid.
Figure 2.6 Effect of acetic acid addition in hydrothermal pretreatment on the pH of the liquid product.

One reason the measured pH could be higher than expected is that greater amounts of water may be produced with the addition of acetic acid. Several studies have suggested that dehydration of the biomass is one of the main mechanisms for removal of O and H from the solid product to improve its fuel value. In particular, production of 5-HMF, one of the major precipitates of the process, is formed through dehydration reactions (Knezevic et al., 2010; Yu et al., 2008). Thus, one effect of acetic acid addition may be the production of water in the reaction scheme. Alternatively, when more acetic acid is present initially, reaction products produced in greater amounts may reduce the activity
coefficient of acetic acid, causing a higher pH reading. However, looking at the actual concentration values is likely to shed more light on the unexpectedly high pH values.

The actual amounts of acetic acid in solution per g of pine after reaction as a function of added acetic level was calculated from HPLC measurements, also shown in Figure 2.6. In all cases where acetic acid is added, no additional acetic acid is produced. When acetic acid is added, less acetic acid exists at the end of the reaction than at the beginning. Obviously, decomposition or consumption of acetic acid must occur when it is present in the reaction scheme. Acetic acid may decompose under the reaction conditions to methane and carbon dioxide. Indeed, when a control run of acetic acid solution only (without biomass) of initial pH 2.09 is subjected to 230 °C hydrothermal carbonization conditions, a release of gas and a pH rise to 2.13 is noted afterward. The same effect of acetic acid reduction is found when 0.4 g acetic acid is added per g of raw corn stover under hydrothermal pretreatment at 195°C (Xu and Thomsen, 2010). When acetic acid is added to the reaction, the same amount may decompose while less is formed, so that a net loss of acetic acid is experienced.

One explanation for acetic acid not being produced when initially added to the process is that the reactions to produce acetic acid could be reversible reactions, with added acetic acid pushing the equilibrium towards less than expected acetic acid production. Glucose, a product of cellulose degradation, further reacts to form acetic acid, as well as formic and lactic acids (Yoshida et al., 2005). With addition of acetic acid, glucose may decompose to other products instead. Indeed, when 0.4 g acetic acid per g pine is added, the reaction produces more than 7 times as much lactic acid as compared to a standard
run. Decomposition of hemicellulose occurs by 230 °C (Yan et al., 2010) and significant production of acetic acid is thought to result from the acetyl groups originally existing in hemicellulose molecules (X. Lu et al., 2009; Yoshida et al., 2005). One source of acetic acid is likely acetylated glactoglucomannans, the main hemicellulose in most softwood species (Xu et al., 2010). Detachment of acetyl groups from hemicellulose to form acetic acid may be a reversible reaction. If addition of acetic acid causes less acetyl groups to be removed from the hemicellulose, so that it is less reacted, more hemicellulose might be expected to remain in the final product. More hemicellulose does remain when acetic acid is added (Figure 2.4). Thus, a shifting of equilibrium reactions, formation of alternative products, and decomposition of acetic acid under the altered conditions may explain the less than expected end concentrations of acetic acid and the increased pH.

The pH values of the liquid product when different levels of LiCl were added are shown in Figure 2.7. These values were measured before any washing water was added. Because pH is defined as \(-\log(a_{H^+})\) and activity equals the activity coefficient \(\gamma\) times concentration, \(\gamma\) obviously can play a major role in what pH is measured. Adding a neutral salt, such as LiCl, can decrease the pH significantly (McCarty and Vitz, 2006). In a standard reaction, about 0.03 g of acetic acid is generated per g of pine (Yan et al., 2010). In a solution containing approximately that amount of acetic acid plus 1 g of LiCl in 5 g of water the measured pH was 1.5. When 2 g of LiCl was added to a solution with the expected amount of acetic acid for a standard run, pH was 0.75. These pH values are higher than those produced in the reactions, which were 1.3 for 1 g LiCl added and 0.56 for 2 g LiCl added per g pine. Thus, when no acetic acid is added, more acid is produced
when LiCl is added than is produced in the standard pretreatment. Clearly, LiCl exerts a catalytic effect in the decomposition of cellulose (Marson and El Seoud, 1999; Tosh et al., 2000) and in the production of higher levels of acid in the solution produced by the hydrothermal carbonization of biomass.

Figure 2.7 Effect of lithium chloride addition in hydrothermal pretreatment

In the runs where both 0.4 g acetic acid and 1 g LiCl were added per g pine, pH at the end without washing water was 1.08. This corresponded exactly to the pH (1.09) for a solution of 0.4 g acetic acid plus 1 g LiCl in 5 g water with no biomass. Since the pH is the same, it is likely that the same amount of acid was produced as was consumed in the process. As discussed previously in this section, when acetic acid is added to the initial reaction solution, no additional acetic acid is produced and acetic acid is consumed. However, adding LiCl does cause acid production. When both are added, there is apparently no net acid production since the pH remains the same. If both 0.4 g of acetic
acid and 1 g of LiCl per g pine are added to the process, HHV increases by 30% compared to the standard process, and the acetic acid level remains the same, so that the end solution could be recycled to treat new batches. Engineers with an interest in using these additives in hydrothermal carbonization could devise a separation and recycle scheme to optimize the overall efficiency of the process.

2.4. Conclusions

Addition of acetic acid and/or LiCl to hydrothermal carbonization of lignocellulosic biomass contributes to increased fuel density of the solid product. HHV is increased and mass yield is reduced when 0.4 g of acetic acid is added per g pine. Addition of LiCl reduces reactor pressure and increases the energy densification ratio. Added at a ratio of 1 g LiCl per g pine, LiCl addition results in greatly increased HHV and reduced mass yield. Cellulose degradation is promoted by the addition of acetic acid and/or LiCl, while energy yield is relatively independent of the additives.

Publication

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2.5 References


Ehrman, T., 1994. Standard method for ash in biomass, laboratory analytical procedure #005, ASTM.


Chapter 3

Effect of Salt Addition on Hydrothermal Carbonization of Lignocellulosic Biomass

As a renewable non-food resource, lignocellulosic biomass has great potential as an energy source. If pretreated with hydrothermal carbonization, the resulting biochar is hydrophobic and of higher energy density. When Ca salts are added to this pretreatment and the Ca impregnated biochar is blended with coal, the Ca can remove SO$_x$ and NO$_x$ produced by coal combustion for energy. Adding salt to this high pressure pretreatment also reduces reaction pressure. Ca propionate, Ca acetate, Mg acetate, Ca lactate, Li chloride, Ca chloride, and Ca formate were tested in hydrothermal carbonizations at 260°C for 5 min. Ca chloride and Ca lactate were found be Ca salts whose addition increases HHV and which decrease pretreatment pressure.

3.1. Introduction

Producing electrical energy using coal has been customary in countries which possess this fossil fuel. While inexpensive to mine, coal has challenges associated with its use. As a fossil fuel, it is limited in quantity and cannot be used alone indefinitely. In addition, in many parts of the world, coal is high sulfur and its burning causes severe
pollution problems, such as acid rain, fine particulates, smog, and high ground-level ozone concentration (Atal et al., 1995, Nimmo et al., 2004). A method to decrease the amount of coal used in power plants by co-firing with a renewable fuel would delay depletion of coal supplies. As other fossil fuels, such as crude oil, diminish, coal may become an increasingly valuable platform feedstock to produce needed chemicals.

Lignocellulosic biomass is a renewable material which can be used to generate electrical energy. It is extremely low in sulfur (Dermirbas, 2004, Madhiyanon et al., 2009) and widely available according to the “2011 U. S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry.” If lignocellulosic biomass is used in conjunction with coal for combustion in power plants, less coal would be required, so that coal resources could be reserved for future uses. In addition, less SO\textsubscript{x} would released into the atmosphere, reducing acid rain compared to using pure coal. However, raw biomass presents some difficulties in processing for use in power generation.

Challenges in the use of raw lignocellulosic biomass include its wide diversity of form and processing methods, decomposition during the storage necessary because of different harvesting times and locations, transportation problems due to biomass particle size variation, and especially its low fuel value compared to coal. The many types of lignocellulosic biomass include hardwood, softwood, corn stover, switchgrass, rice hulls, and bagasse. While raw wood is readily available most seasons of the year, it has a high moisture content, still is subject to decomposition, and needs high energy milling to be reduced to a small particle size if co-firing with coal is desired. Less milling is required for corn stover or bagasse, but they are even more biodegradable, and corn stover is also
harvested seasonally. Seasonally harvested rice hulls and switchgrass have their own transportation and processing challenges, which include small harvested particle size.

Solutions to the challenges of lignocellulosic biomass use are found in pretreatments for raw biomass. Many pretreatments have been investigated, including mechanical pretreatment (milling to increase surface area), strong or dilute acid pretreatment, alkaline pretreatment, oxidative pretreatment, ammonia (AFEX) pretreatment, supercritical carbon dioxide pretreatment (which increases pore size), steam pretreatment, steam explosion (with a more rapid depressurization and cooling), dry pyrolysis, and hydrothermal carbonization (Hendriks and Zeeman, 2009; Lynam et al., 2011; Yan et al., 2009). Of these many pretreatments, hydrothermal carbonization (HTC), or wet torrefaction, performed after milling will be discussed primarily.

In the HTC pretreatment, milled biomass is immersed in subcritical water and heated to temperatures between 200 and 300°C at pressures high enough to maintain liquid water for 1 to 30 min. Expensive drying of the biomass is not required in this process. Yan et al. (2009, 2010) have found HTC to remove hemicellulose and some cellulose, leaving high fuel value lignin as its solid product (biochar), which solves lignocellulosic biomass’ low fuel value problem. HTC of varying lignocellulosic biomass also produced a friable, homogenized biochar, similar despite differing feedstocks. In addition, HTC increases the hydrophobicity of biomass, causing it to decompose much more slowly (Acharjee, 2010). The friable product can be pelletized, making a stable, uniform substance to transport for co-firing with coal (Reza, 2011). However, as HTC is a high pressure process, requiring thick reactor walls and arduous safety procedures. An
additive to HTC pretreatment could partially alleviate this difficulty. If this additive could also reduce the SOx produced when biochar is co-fired with coal, it might be a valuable addition to the HTC process.

Thermodynamics indicate that if a soluble salt is added to water the vapor pressure of the mixture is lowered. Depending on how hydrophilic the salt is, a higher or lower vapor pressure depression may be seen. Previously, the addition of LiCl in the HTC process has been found to decrease the process’ pressure (Lynam et al., 2011). Unfortunately, neither Li nor Cl has been shown to decrease SOx in the thermoconversion of coal.

In coal furnaces, Ca plays a dominant role in retaining SOx in the ash that remains after combustion (Cheng et al., 2003). Ca catalyses the combustion of synthetic chars (Levendis et al., 1989), and greater catalytic effects are observed for calcium compared to magnesium (Atal et al., 1995). Nimmo et al. (2004) have described the reaction scheme for coal with calcium magnesium acetate added. At temperatures over 900°C, calcium magnesium acetate (CaMg\(_2\)(CH\(_3\)COO)\(_6\)) decomposes to CaO, MgO, and CH radicals. In the presence of SO\(_2\), CaO and MgO convert to CaSO\(_4\) and MgSO\(_4\), removing SOx from the flue gases. At lower O\(_2\) levels, CH radicals react with NO to produce HCN and then N\(_2\), thus removing NOx from the flue gases. A Ca/S ratio of about 2 was found to be effective in removing SO\(_2\). However, Calcium magnesium acetate is quite expensive (Niu et al., 2011). Calcium propionate and calcium acetate have also been found to reduce NO and SO\(_2\) in coal fired flue gas (Niu et al., 2011).
There could be advantages to adding various Ca or Mg salts in coal combustion on NO and SO2 reduction. If these salts are added in HTC pretreatment of lignocellulosic biomass, reducing the process pressure, and then the pelletized biochar is added to the coal, SOx and NOx could be removed from the combustion gases. In the present study, various Ca salts, as well as Mg acetate, were added to the HTC process to investigate their pressure reduction and effect on higher heating value (HHV) and mass yield.

3.2. Material and Methods

3.2.1 Biomass

As a representative lignocellulosic biomass, loblolly pine was acquired from Alabama, USA. On a mass basis, it consists of 11.9 % hemicelluloses, 54.0 % cellulose, 25 % lignin, 8.7% extractives and 0.4% ash (Yan et al., 2010). Pine samples were milled to the desired particle size of 14-28 mesh (1.168 to 0.589 mm in diameter) before hydrothermal carbonization. Moisture content has been measured to be 5.2 % by weighing a sample, then measuring weight loss after drying for 24 h at 105 °C (Lynam et al., 2011).

3.2.2 Salts

Ca propionate, Ca acetate, and Ca formate were obtained from MP Biomedicals, LLC (Solon, OH, USA). Mg acetate tetrahydrate, Ca lactate pentahydrate, and Ca chloride were obtained from Fisher Scientific (Fairlawn, NJ, USA). Mg acetate tetrahydrate and Ca lactate pentahydrate are referred to as Mg acetate and Ca lactate, respectively in the remainder of this work for brevity. Li chloride was obtained from Alfa
Aesar. All salts, except LiCl and CaCl₂, were dissolved by stirring 8 g into 40 g deionized water, so that 1 g of each salt was added per g of pine for a hydrothermal carbonization reaction. For the chloride salts, only 7 g of salt were stirred into 35 g of deionized water, and 7 g of biomass was used instead of 8 g. Reduced amounts of reactants were used because of the space in the reactor taken up by the glass liner used with the chloride salts to prevent pitting in the metal reactor.

3.2.3 Hydrothermal carbonization

Hydrothermal carbonization of loblolly pine was performed in a Parr Series 4560 bench-top reactor of volume 100 mL (Moline, IL). For each run, loblolly pine was placed in the reactor and either deionized water (as the control) or a salt solution with 1 g of salt per g of biomass was poured in the reactor to cover the biomass. In all runs, water to loblolly pine mass ratio was 5:1. A glass liner was placed in the reactor for the LiCl and CaCl₂ runs to protect reactor walls from pitting. After the reactants were loaded, the reactor was purged with nitrogen for 10 minutes to remove oxygen. Heating time from room temperature to 180°C required about 20 minutes, while about 10 more minutes were required to heat the reactor to 260°C. The glass liner did not significantly affect the heating rate. Reaction time was 5 minutes after 258 °C was reached, after which the reactor was rapidly cooled by immersion in an ice bath. After immersion, the internal reactor temperature cooled to below 180°C in less than 1 minute at a rate of approximately 2 K/s, and subsequently cooled to room temperature. The temperature of the reactor was held at 260°C using a PID controller. The reactor pressure was not
controlled, but was measured when 258 °C was initially reached. For the run without salt added, pressure corresponded to the saturated vapor pressure.

3.2.4 Quantitative measurement of reaction products

After cooling the reactor to 25 °C, the gas product was released without further evaluation. The liquid portion and the hydrothermally carbonized solid were separated by vacuum filtration using a Buchner funnel with Whatman filter paper (Grade 3, 0.6 µm). In all experiments, 6.25 g rinse water per g loblolly pine was added for enhanced recovery from the reactor. The solid product was dried at 105 °C for 24 h.

3.2.5 Analyses

The pH of the liquid portion was measured using a digital probe. Accuracy in pH measurement was approximately ± 0.05 for experiments involving the salts, probably due to acid error, a time dependent phenomena (McCarty and Vitz, 2006).

Ash analysis in triplicate was performed on all solid samples in which salts were added to the reactants. After drying for 24 h at 105 °C, 1 g of the pretreated solid was heated to 575 °C in a muffle furnace and maintained at that temperature for at least 12 h to ensure that only ash remained. Samples were cooled to room temperature in a desiccator before being re-weighed to determine ash percentage (Ehrman, 1994). For the no salt run ash was considered to be 0.4% (Yan et al., 2009).

Heats of combustion (HHV) for both raw loblolly pine and pretreated solid product (biochar) were measured in a Parr 1241 adiabatic oxygen bomb calorimeter fitted with
continuous temperature recording. Samples (0.2 g) were dried at 105 °C for 24 h prior to analysis.

3.3. Results and Discussion

3.3.1 Effect of salt addition on mass yield

The mass yield is the fraction of solid product (biochar) that remains after the hydrothermal carbonization (HTC) process, compared to the original dried biomass. In this case mass yield was calculated on an ash-free basis, since some of the salt precipitates onto the biochar. Compared to the control with no salt added, the hydrothermal carbonizations with Ca propionate, Ca chloride, or Ca formate added had slightly increased mass yield, as shown in Figure 3.1. This indicates that a lesser proportion of the biomass was removed with HTC when these salts were added. The hydrothermal carbonization with Ca acetate showed the same mass yield. The salts Mg acetate, Ca lactate, and Li chloride displayed mass yields lower than the no salt added control, indicating greater biomass removal (Figure 3.1) In HTC, hemicelluloses are removed most rapidly and completely, cellulose is the next most quickly to be solubilized, and lignin is relatively inert (Reza, 2011). Hemicelluloses and cellulose have lower higher heating values (HHV) than lignin, so that the more they are removed from the biomass, the greater its HHV.
Effect of salt addition on energy densification

Energy densification is the ratio of the HHV of the biochar to that of the original raw biomass. Figure 3.2 shows the energy densification of each of the runs with salt added, compared to the no salt control. The standard procedure, with no salt added, increases the HHV by 35% at 260°C, compared to the raw loblolly pine. Ca formate shows a lower densification. Its lower HHV probably correlates to its higher mass yield, which indicates that less hemicelluloses and cellulose is removed from the biomass, leaving a higher proportion of these components compared to lignin. A higher proportion of lignin gives a greater HHV. Ca propionate, Ca acetate, and Mg acetate additions show energy densifications similar to the control, thus indicating that these salts neither assist nor...
hinder the hydrothermal carbonization. Ca lactate, Li chloride, and Ca chloride addition significantly increase the energy densification compared to the no salt added control. Chloride ions are known to disrupt the hydrogen bonding between adjacent cellulose polymer strands (Marson and El Seoud, 1999; Remsing et al., 2006), facilitating their solubilization and removal from biomass. The lactate may perform a similar action in disrupting cellulose hydrogen bonding. If more cellulose is removed from the biomass, a higher proportion of lignin remains, increasing the biochar’s HHV.

![Energy densification](image)

Figure 3.2 Energy Densification Comp. of Reactions w/ Additions of Different Salts

3.3.3 Effect of salt addition on energy yield

Energy yield is the product of mass yield multiplied by energy densification. It is a measure of the fraction of energy from the raw biomass that remains in the biochar product. Figure 3.3 shows the energy yields from each of the hydrothermal carbonizations. Ca propionate, Ca acetate, and Ca formate addition gives energy yields
similar to that of the no salt added control. Mg acetate, Ca lactate, and Li chloride additions to the hydrothermal carbonization process cause somewhat lower energy yields. Ca chloride gives a surprisingly high energy yield of over 0.9. Ca chloride, with 2 chloride atoms per molecule, must interact with the biomass so as to remove only low HHV components, while leaving lignin and other high HHV components unchanged, so that mass yield and energy densification are both high.

Figure 3.3 Energy Yield Comparison of Reactions with Different Salt Additions
3.3.4 Effect of salt addition on pH

Table 3.1 shows the pH of the liquid product of the hydrothermal carbonizations. Since the no salt added control run starts with neutral de-ionized water, acid must be produced by the reaction to lower the pH of the resulting solution. Yan et al. (2010) have shown that hydrothermal carbonization produces acetic acid, along with smaller amounts of formic and lactic acids. Adding acetate to the reaction scheme may shift equilibrium reactions in which it is involved to the left, so that less acetic acid is formed. This may partially explain the higher pH’s displayed by the solution when Ca acetate and Mg acetate are added. In general, the added salts, except for those with chloride, buffer the solution, so that pH is not decreased as much as would be expected. The presence of chloride ions from Li chloride and Ca chloride enhance the activity of the $H^+$ ions, resulting in greatly lowered pH (Lynam et al., 2011; McCarty and Vitz, 2006). Of the non-chloride salts, Ca lactate shows the lowest pH, which may indicate a greater extent of reaction, with more acid production.

Table 3.1 Effect of Salt Addition on pH, Ash %, and Reaction Pressure

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Ash %</th>
<th>P (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No salt added</td>
<td>2.97</td>
<td>0.4</td>
<td>4.20</td>
</tr>
<tr>
<td>Ca propionate</td>
<td>4.84</td>
<td>5.2</td>
<td>3.90</td>
</tr>
<tr>
<td>Ca acetate</td>
<td>4.64</td>
<td>7.4</td>
<td>3.95</td>
</tr>
<tr>
<td>Mg acetate</td>
<td>4.38</td>
<td>1.9</td>
<td>4.00</td>
</tr>
<tr>
<td>Ca Lactate</td>
<td>3.79</td>
<td>4.0</td>
<td>3.95</td>
</tr>
<tr>
<td>LiCl</td>
<td>1.28</td>
<td>1.2</td>
<td>3.00</td>
</tr>
<tr>
<td>CaCl2</td>
<td>1.54</td>
<td>6.8</td>
<td>3.48</td>
</tr>
<tr>
<td>Ca formate</td>
<td>4.50</td>
<td>1.3</td>
<td>4.10</td>
</tr>
</tbody>
</table>
3.3.5 Effect of salt addition on reaction pressure

Maintaining liquid water at a temperature of 260°C requires high pressures. The vapor pressure of pure water at 260 °C is 4.7 MPa. (http://www.kavelaby.npl.co.uk/chemistry/3_4/3_4_2.html, accessed November 11, 2011). An aqueous LiCl solution at 260 °C has been shown to have a vapor pressure of 3.4 MPa for the same mole fraction as the experiment conditions used in this study (Fedorov et al., 1976). Vapor pressure of a CaCl₂ – water solution at 250 °C has been measured to be 3.7 MPa for the same mole fraction as our study used experimentally (Jiang and Pitzer, 1996). Although some vapor pressure data on water solutions saturated with Ca lactate, Ca acetate, and Mg acetate has been reported near room temperature (Apelblat et al., 2005; Apelblat and Korin, 2001), none is available at temperatures above 90 °C. No high temperature vapor pressure data is available for Ca propionate or Ca formate solutions with water.

Table 3.1 displays the pressures for the 260°C hydrothermal carbonizations, with and without salt addition. As expected, adding salt reduces the reaction pressure. The more hygroscopic salts, Li chloride and Ca chloride, show markedly lower reaction pressure, 30% lower for LiCl and 20% lower for CaCl₂. Except for Ca formate, whose pressure reduction is minimal, the other salts reduce pressure by about 7%. Pressure reduction in 260°C hydrothermal carbonizations improves safety in operation and reduces the reactor costs. However, chloride ions can cause pitting in some metal reactors, so that glass lining may be required.
3.4. Conclusions

Adding Ca lactate, Li chloride, and Ca chloride to the hydrothermal carbonization pretreatment of loblolly pine enhanced the reactions occurring so that the resulting biochar had increased HHV compared to that with no salt added. Since Ca salts have been shown to reduce SO$_x$ and NO$_x$ emissions from coal thermal conversion processes, and adding renewable biomass to coal can decrease the amount of the fossil fuel depleted, adding biomass treated with Ca salts may be of great advantage. Inexpensive Ca chloride showed a particularly high energy yield and a large reduction in hydrothermal carbonization pressure. If a Ca salt without chloride is desired, Ca lactate showed a high energy densification and some pressure reduction when added to the hydrothermal carbonization process.

Acknowledgements

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3.5 References


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Preliminary Study of the Effect of Ionic Liquid Dissolution of Rice Hulls

As a highly available waste product, rice hulls could be a starting block in replacing liquid fossil fuels. However, their silica covering can make further use difficult. This preliminary study investigates effects of dissolving rice hulls in the ionic liquids 1-ethyl-3-methylimidazolium acetate (EMIM Ac), 1-hexyl-3-methylimidazolium chloride, (HMIM Cl), 1-butyl-2,3-dimethylimidazolium chloride (BBMIM Cl), and 1-allyl-3-methylimidazolium chloride (AMIM Cl), and what lignocellulosic components can be precipitated from the used ionic liquid with water and ethanol. EMIM Ac at 110°C for 8 h was found to completely remove lignin from rice hulls, while ethanol was capable of precipitating lignin out of the used EMIM Ac.

4.1. Introduction

Rice hulls are an underutilized and highly available resource in our world. According to the International Rice Research Institute, rice is the staple food for more than half of the world’s population. The Food and Agriculture Organization of the United Nations
(FAO, www.fao.org) has estimated the 2010 world production of rice as 700 million tons. Since the hull or husk constitutes 20% of rice, vast quantities of rice hulls are disposed of as waste, or burned in open fields, polluting the environment (Kim et al., 2004). Rice hulls are neither edible by humans nor compete with food crops for arable land. As a lignocellulosic waste product available in huge amounts, they are a potential energy source to replace limited fossil fuel resources.

Rice hulls, as removed from the rice grain, already exist in small thin curved slices so that little milling is necessary, compared to wood. However, the bristles on the outside of the hull consist of a layer of silicified cuticle and the inside concave surface is similarly protected by a coating of silica, which comprises 21% of the husk by weight. A tough layer containing lignin, silica, and other lignocellulosic components comprises the inside (Ouyang, 2001). The silica “armor” protecting other components makes rice hulls difficult to compost or process in other ways. While they can be made into panel boards, these have been found to have undesirable properties (Chen, 1979). Rice hull ash is considered to be a potentially valuable product, with the silicon extracted from it being useful for many purposes such as molecular sieves, catalyst supports (Bansai et al., 2006), photocatalysts (Artkla, 2009), and adsorbents to remove metal ions (Wang, 2008). Rice hull lignin has been found to consist mostly of guaiacyl and p-hydroxyphenyl units (Salanti et al., 2010). The hemicellulose from rice hulls is composed mostly of xylan (Watanabe et al., 1983).

Separation of individual lignocellulosic biomass components, such as cellulose or lignin can increase their value dramatically. Cellulose, if not combined with lignin, can
be converted into the biofuel ethanol through hydrolysis and subsequent fermentation or used as a platform chemical for paper or polymers. Pure lignin can be used to make aromatics, as well as being a high energy density fuel. However, separating lignocellulosic biomass into its constituent components can be difficult. The Kraft process for paper is one example. Such processes generally have required strong acids or alkalis or high temperatures and pressures, making them expensive and energy intensive, although some useful biological pretreatments have been found (Yu et al., 2009). But a new “green” class of solvents has recently been discovered with applications to lignocellulosic biomass. Ionic liquids (ILs) have novel abilities to dissolve cellulose and lignin both separately and as packaged in biomass.

Ionic liquids are molten salts with melting temperatures of 100 °C or lower. The cation of these ionic pairs is typically large, so that the pair is poorly coordinated, which causes the aggregate to be liquid at much lower temperatures than common salts. Since the turn of this century, some ionic liquids have been found which dissolve lignocellulosic materials. Swatloski et al. (2002) first determined that micro crystalline cellulose could be dissolved by the ionic liquid 1-butyl-3-methylimidazolium chloride.

A wide variety of ionic liquids has since been found to dissolve cellulose at least partially (Fukaya et al., 2006; Lateef et al., 2009; Vitz et al., 2009; Zhang et al., 2005; Zhao et al., 2009). In general, temperatures of between 80-120 °C and stirring are used in the process, with dissolution times varying from 20 min to 24 h. Higher temperatures and longer duration aid in dissolution, but may result in degradation of the cellulose and the IL (Sun et al., 2009). The mechanism for cellulose dissolution has been investigated
by NMR (Remsing et al., 2006) which indicated it was caused by hydrogen bonding between an IL’s Cl\(^-\) anion and cellulose’s hydroxyl protons. Determining which IL to use for cellulose dissolution is a difficult decision. Imidazolium cations with various side groups combined with anions such as Cl\(^-\), acetate, or formate appear to be most effective in dissolving cellulose. (Maki-Arvela et al, 2010). Cations and anions which are too bulky seem to be ineffective in cellulose dissolution. Vitz et al. (2009) showed that when odd numbered carbon chain arms are added to imidazolium cations with Cl\(^-\) anions, cellulose solubility was greatly reduced compared to even C chain additions, probably due to bulkiness from the morphology change or stearic hindrance. They also determined that carbon side chains longer than 6 caused decreasing solubility. Thus far the most useful parameter to use in choosing an IL appears to be the β Kamlet-Taft solvent polarity parameter (Doherty et al., 2010). Another challenge is the high viscosity of some ILs, which can be mitigated by replacing a Cl\(^-\) or acetate anion with a formate anion (Fukaya et al., 2006).

After dissolution in an IL, cellulose can be regenerated from the solution by the addition of an excess of water or other solvents. A hydrodynamic shell of water molecules surrounds the IL’s ions, permitting the cellulose intra and intermolecular hydrogen bonds to re-form (Zavrel et al., 2009), so that a cellulose precipitate is produced. Zhang et al. (2005) demonstrated that 8 wt% of cellulose could be dissolved in 1-allyl-3-methylimidazolium chloride (AMIM Cl) at 90 °C and then regenerated by water addition to produce a cellulose film similar to cellophane. Another reason to regenerate
cellulose using an IL is that such cellulose has been shown to be less crystalline and thus easier to hydrolyze enzymatically (Zhao et al., 2009).

Lignin is the second most abundant component of biomass existing in our world, after cellulose. As separated from lignocellulosic biomass by the Kraft process, it has been used for fuel, binders, dispersants, and emulsifiers and could have many other applications in the polymer industry (Pu, 2007). The ability of ILs to dissolve lignin is of great interest. Pu (2007) found Kraft lignin in 1,3-dimethylimidazolium methylsulfate (MMIM MeOSO₃) to have a solubility of 344 g/liter at 50 °C. Kraft lignin was determined to have a solubility of >300 g/kg in both 1-ethyl-3-methylimidazolium acetate (EMIM Ac) and 1-allyl-3-methylimidazolium chloride (AMIM Cl) at 90 °C when stirred for 24 h (Lee et al., 2009). Lee et al. (2009) have also suggested that the Hildebrand solubility parameter can predict which ILs would be most suitable in dissolving lignin.

Not only dissolution, but also regeneration of lignin is needed if expensive ionic liquids are to be recycled for further use. Using two different ILs and a mixture of lignin and cellulose, Lateef et al. (2009) found that a separation of cellulose and lignin was possible by first regenerating cellulose by adding water, then evaporating the water and adding ethanol to precipitate lignin. However, when a third IL was used both solvents produced a precipitate mixture of lignin and cellulose.

Working only with ILs and biomass components has limited usefulness. Of greater worth is examining the effect of ILs on actual lignocellulosic biomass. Many studies have probed the solubilities of lignocellulosic biomass itself (Doherty et al., 2010; Fort et al., 2007; Kipelainen et al., 2007; Li, B. et al., 2010; Li, C. et al., 2010; Pezoa et al.,
As expected, dissolving cellulose or lignin embedded in biomass is a much more difficult problem than using pure cellulose or lignin. Lee et al. (2009) determined that while > 100g per kg of cellulose could be dissolved in EMIM Ac at 80 °C, the solubility of maple wood flour was <5g per kg at the same temperature. Although MMIM MeOSO₃ dissolves lignin well, as described above, it does not dissolve maple wood flour at 80 °C even after 24 h (Lee et al., 2009). Determining the correct temperature for dissolution appears to be essential when working with lignocellulosic biomass.

The structure of lignocellulosic biomass makes it stable and recalcitrant to chemical or biological damage. The long polymer chains of cellulose are hydrogen bonded together length-wise in microfibrils, then bundled together in macrofibrils which give rigidity to cell walls. These cellulose bundles are packaged inside a sheath of lignin and hemicellulose to form plant cell walls (Mosier et al., 2005). The plant cells are glued together by the middle lamella, an area of high lignin content. Lignin is resistant to chemical attack, requiring strong acids or alkalis to cleave the crosslinks holding it together. It forms a protective shield preventing use of the valuable cellulose inside the lignocellulosic package.

Using ILs on lignocellulosic biomass is valuable because a renewable source of cellulose for polymers or for enzymatic hydrolysis to glucose can be obtained simultaneously with a renewable source of lignin, a possible platform chemical. Two ILs stand out for their ability to dissolve lignocellulosic biomass. Zavrel et al. (2009)
determined that at 90 °C AMIM Cl could dissolve completely 5 wt % of four types of wood chips in 12 h, while EMIM Ac could dissolve completely under the same conditions spruce, common beech, and chestnut. However, only a few of many other ILs with possible efficacy on biomass have been investigated and reported.

The goal of the present study is to determine the effects of ILs on rice hulls, a lignocellulosic biomass little investigated with ILs thus far. Two ILs commonly used on lignocellulosic biomass, 1-ethyl-3-methylimidazolium acetate (EMIM Ac) and 1-allyl-3-methylimidazolium chloride (AMIM Cl) have been applied to rice hulls in this study. In addition, two more atypical and less expensive ILs, 1-hexyl-3-methylimidazolium chloride, (HMIM Cl) and 1-butyl-2,3-dimethylimidazolium chloride, (BBMIM Cl), have been chosen for investigation to determine their effects on rice hulls.

4.2. Materials and methods

4.2.1 Materials

The ionic liquids 1-ethyl-3-methylimidazolium acetate, >90%, (EMIM Ac), 1-hexyl-3-methylimidazolium chloride, >97.0%, (HMIM Cl), 1-butyl-2,3-dimethylimidazolium chloride, >97.0%, (BBMIM Cl) and 1-allyl-3-methylimidazolium chloride, >97.0%, (AMIM Cl) were obtained from Sigma Aldrich (sigmaaldrich.com). Molecular structures of the ILs are shown in Fig. 4.1. Rice hulls were obtained from California, USA. Nylon membrane filters, 20 micron, were obtained from Sterlitech (Kent, WA, USA). Kraft lignin (alkali), cellulose fibers (medium), and xylan (from beechwood) was obtained from Sigma Aldrich (sigmaaldrich.com).
4.2.2 Dissolution of rice hulls in ionic liquids and regeneration of precipitates

Rice hulls were ground in a household blender and meshed in sieves. Those between 1.168 and 1.651 mm were selected and dried in a 105 °C oven for at least 24 h. The chosen ionic liquid was also dried in a 105 °C oven for 24 h. One gram of dried rice hulls were placed in 10 g of ionic liquid in a beaker suspended in an oil bath for 4 or 8 h, with magnetic stirring. The oil bath was manually controlled to be 90 °C or 110 °C using a hot plate. A schematic of the process is shown in Fig. 4.2.
The pretreated rice hulls were separated by vacuum filtration using a dried nylon filter. They were then magnetically stirred with 40 ml deionized water at \( \sim 50 ^\circ C \) for 45 min to remove any IL clinging to the hulls. The filtrate was also stirred with \( \sim 4x \) its volume of deionized water at \( \sim 50 ^\circ C \) for 45 min. A dried nylon filter was used to collect with vacuum filtration the water precipitate from the diluted filtrate. The previous procedure was repeated in some cases, if collection was slow. A nylon fish net filter was used to remove the pretreated rice hulls from the water they had been stirred in, using vacuum filtration. For BDMIM Cl and AMIM Cl, all filtration was performed in a manually controlled muffle furnace at approximately 105 °C and 85 °C, respectively, to decrease the viscosity of the filtrate, and prevent crystallization of the IL. The rice hulls and water precipitate were dried in a 105 °C oven for 24 h.
The filtrate resulting from the water precipitation was dried in a vacuum oven set at ~95 °C. After 10 days (to give a constant filtrate weight), the filtrate was considered dry. For EMIM Ac and HMIM Cl, 4 times the filtrate’s volume of ethanol (>95%) was added to ensure that a hydrodynamic shell of ethanol molecules surrounded the IL’s ions, so that dissolved lignocellulosic components would be precipitated. The diluted filtrate was placed in a refrigerator at 4 °C overnight. Vacuum filtration with a dried nylon filter was performed to collect the ethanol precipitate.

4.2.3 Analyses

4.2.3.1 Fiber analysis

For pretreated rice hull samples, fiber analysis was carried out using a modified Van Soest method using the ANKOM A200 Filter Bag Technique (Goering and Van Soest, 1970). Solid product samples (~0.2 g) were dried at 105 °C for 24 h. After placement in sealed filter bags, samples were digested with neutral detergent to determine neutral detergent fiber (NDF). Digestion with 1 N sulfuric acid detergent determined acid detergent fiber (ADF), and subsequent digestion in 72 % sulfuric acid gave a value for acid detergent lignin (ADL). The weight percentage extracted by neutral detergent (NDF) is considered to be aqueous solubles. The difference of the NDF - ADF percentage yields the percentage of hemicelluloses, while ADF – ADL is considered to be the percentage of cellulose. The weight remaining after the ADL procedure is considered to be lignin plus ash. Fiber analysis is generally accurate + or – 5%. Some difficulties exist in fiber analysis of rice hulls pretreated in ionic liquids (ILs). Although any remaining IL would be expected to exit biomass as aqueous solubles, ILs are strongly
attracted to and hydrogen bond with lignocellulosic components such as cellulose (Guo et al., 2010a, 2010b), and may be difficult to remove. If an IL remains in what is considered the cellulose fraction of the biomass, an inflated estimate of the percentage of cellulose remaining in the pretreated biomass may be calculated.

The percentage of lignocellulosic components removed were determined by taking the initial mass of the sample and multiplying by the % given for rice hulls by fiber analysis to give the original mass of a given component, then subtracting the final mass of the pretreated sample multiplied by the % of the component given by fiber analysis. This quantity is the mass of the component removed by pretreatment. After dividing by the original mass of a given component, the % removed is determined.

4.2.3.2 Thermogravimetric analysis

An STA-6000 from Perkin Elmer (MA, USA) was used to determine the thermal behavior of the raw and pretreated rice hulls. Samples were dried at 105°C for 24 h prior to the TGA analysis. Samples between 9-15 mg were placed into the sample chamber. Air at 20 ml/min was charged to permit combustion of the samples. The heat program applied was from 30-105 °C at a rate of 50°C/min, then a hold for 10 min, then temperature increase at 50°C/min to 900 °C, then a hold for 10 min. Ash fraction was calculated as the final mass divided by the dried original mass. The ash content of raw rice hulls was also measured using a standard method for ash in biomass. After drying for 24 h at 105 °C, 1 g of the raw rice hulls was heated to 575 °C in a muffle furnace and maintained at that temperature for at least 12 h to ensure that only ash remained. Samples were cooled to room temperature in a desiccator before being re-weighed to
determine ash percentage. The ash percentages yielded by both methods for raw rice hulls were within ±2%.

4.2.3.3 Precipitate analysis

The water and ethanol precipitates from the 110 °C and 8 h separations were estimated by putting a sample (0.004-0.050 g) that had been dried for 24 h at 105 °C in an ANKOM A200 filter bag. The bags were weighed and then placed in deionized water at approximately 85 °C with magnetic stirring for 45 min. After overnight drying at 105 °C, the bags were re-weighed, and the mass lost considered to be hemicellulose and aqueous solubles. The same bags were then placed in 25 °C 72% H₂SO₄ with magnetic stirring for 1 h. After overnight drying at 105 °C, the bags were again re-weighed, and the mass lost considered to be cellulose. Remaining mass was considered Klason lignin.

The time period used to remove hemicellulose in this procedure was determined by placing samples containing one half xylan(from beechwood) and one half cellulose fibers in ANKOM A200 filter bags. Six bags were were placed in deionized water at approximately 85 °C with magnetic stirring. After 30 min, two bags were removed, then after 1h and 30 min two more bags were removed, and finally after 2h and 30 min the two last bags were removed. The bags were removed and dried for 24 h at 105 °C and then weighed. A time period more than 30 min but less than 1 h and 30 min appeared to remove all the xylan, but not significant amounts of cellulose. Next a 45 min time period was used for five bags, three with a one third xylan, one third cellulose fibers, and one
third lignin mixture, and three controls containing only xylan, cellulose fibers, or lignin.
The 45 min time period appeared to remove all the xylan and small amounts of cellulose, but no lignin.

To determine the time period needed to remove lignin, bags containing controls with only cellulose fibers or lignin, were placed in 25 °C 72% H$_2$SO$_4$ with magnetic stirring. After 30 min, after 1h, and after 2 h, a bag originally containing cellulose fibers and a bag originally containing lignin were removed from the 72% H$_2$SO$_4$. A 1 h time period removed all cellulose, and only small amounts of lignin. Lignin removal from 72% H$_2$SO$_4$ treatment may be due to the alkali type of lignin used to develop this process. Lignin removed from biomass by ionic liquids is generally considered to be more “native,” (Lee et al., 2009) and thus less likely to be dissolved by 72% H$_2$SO$_4$ treatment. The procedure described above can only be used to roughly estimate the fractions of lignin, cellulose, and hemicellulose regenerated from ionic liquid treatment. Future studies using larger quantities of biomass and ionic liquids are planned which will permit more exact types of precipitate analysis.

4.2.3.4 Scanning electron microscopy (SEM)

A FE-SEM Hitachi Scanning Electron Microscope (SEM) model S-4700 was used to visualize raw and pretreated rice hulls. Samples of raw rice hulls, and rice hulls pretreated with EMIM Ac at 90 °C for 4 h, 90 °C for 8 h, 110 °C for 4 h, and 110 °C for 8 h were used for SEM images. The samples were maintained on special studs and platinum coated with polaran coater tar 5000, under an argon atmosphere for a coating
4.3. Results and discussion

4.3.1 Mass yield from ionic liquid pretreatment precipitates

Fig. 4.1 shows the structure and melting points of each of the ionic liquids (ILs), while Fig. 4.2 illustrates the pretreatment process. The combined weight of the washed and then dried precipitates from both water and ethanol treatments from each run is considered to be the mass removed from the original rice hull samples. Fig. 4.3 shows the percentage of mass removed by both water and ethanol precipitations for each ionic liquid under each pretreatment condition.

a)
b) Mass % removed by precipitates after HMIM Cl treatment

Mass % removed by precipitates after BDMIM Cl treatment

90°C
110°C
4.3.1.1 Mass yield from EMIM Ac pretreatment precipitates

EMIM Ac, the only non-Cl IL studied here, removes approximately 10% of the original mass as precipitate regardless of the length of time or temperature of the separation as shown in Fig. 4.3a. It is possible, however, that other precipitating solutions, such as methanol, 2-propanol, acetone, dichloromethane, chloroform, acetonitrile, and tetrahydrofuran (Maki-Arvela et al., 2010) could remove more precipitate from the EMIM Ac solution after pretreatment. In addition, precipitate losses due to washing would be expected to occur (Sun et al., 2009). The precipitate removed when water is added to the IL filtrate from the 110 °C and 8 h separation has been estimated, using the ANKOM A200 filter bag method, to be approximately half cellulose and half
hemicellulose. The precipitate removed with ethanol at the same conditions appears to be approximately half lignin and half hemicellulose. Lateef et al. (2009) found water to preferentially precipitate cellulose and ethanol to preferentially precipitate lignin when a lignin-cellulose mixture was solubilized in the ILs 1-propyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium chloride. In the same study, a third IL, 1-(2-cyanoethyl)-3-methylimidazolium bromide precipitated both lignin and cellulose with either water or ethanol. Lignin linked to xylan, the hemicellulose most prevalent in rice hulls (Watanabe et al., 1983), has been found to be more resistant to removal than galactan-linked lignin (Fu and Lucia, 2003). The possibility exists that a xylan chain break, with some xylan remaining attached to lignin and some still attached to an acetate ion-solubilized cellulose, causes the two different precipitate compositions (Kilpelainen et al., 2007). Regardless of the reason for the two different types of precipitates found, the ability to separate lignin from cellulose removed from the rice hulls could be useful, permitting the cellulose-hemicellulose precipitate to be enzymatically hydrolysed to produce glucose and xylose (using xylanases) prior to fermentation (Lee et al., 2009). It must be noted that glucose-xylose mixtures can be co-fermented using a genetically modified Saccharomyces yeast to produce biofuels (Sedlak and Ho, 2004; Zhao et al., 2010). Singh et al. (2009) found that cellulose regenerated after EMIM Ac treatment was efficiently hydrolysable with high sugar yield, requiring only a relatively short duration. The lignin could be easily removed from the lignin-hemicellulose precipitate using a hot water treatment, and the lignin, expected to be pure, could be a source to produce many valuable chemicals. EMIM Ac, since it does not contain Cl− ions, may be more useful as a chemical less hazardous to equipment.
4.3.1.2 Mass yield from HMIM Cl pretreatment precipitates

As shown in Fig. 4.3b, HMIM Cl only removes 5 wt % of the original rice hull mass when it is pretreated at 90 °C for 4 or 8 h. However, when pretreated at 110 °C, about 20% of the rice hull mass is precipitated, which is significantly higher. The increase in temperature would be expected to significantly increase diffusivity of the IL into the silica covering of the rice hull. Diffusivity is a function of both temperature and the inverse of viscosity. Viscosity, however, is also an exponential function of temperature such that, in liquids, it is substantially reduced with increasing temperature. Thus, even only a 20 °C temperature difference could significantly increase diffusivity, increasing the solubilization of the lignocellulosic components. The increase in mass % removal with temperature and time seems to indicate that the dissolution of rice hulls in HMIM Cl is a mass transfer limited process. This is likely considering the armor-like silica coating of rice hulls, which necessitates penetration gain access to the lignocellulosic components within. The precipitate removed when water is added to the IL filtrate from the 110 °C and 8 h separation has been estimated using the ANKOM A200 filter bag method to be approximately one sixth lignin and the remainder cellulose. Thus, this IL behaves more similarly to 1-(2-cyanoethyl)-3-methylimidazolium bromide in the study of Lateef et al. (2009), where both lignin and cellulose were precipitated by water. However, the precipitate with ethanol from the 110 °C and 8 h separation appeared to be comprised of only hemicellulose. These two precipitates could again be used: one with
cellulase and further fermentation with a standard yeast, and the other with a xylase and a xylose compatible yeast, such as Pachysolen tannophilus, Pichia stipitis, or Candida shehate (Schneider et al., 1981; Wang et al., 1980; Zhao et al., 2010).

4.3.1.3 Mass yield from BDMIM Cl pretreatment precipitates

For BDMIM Cl, neither pretreatment temperature nor duration appears to make a significant difference in the wt% removed of the rice hulls (Fig. 4.3c). For all conditions, about 20 wt% is removed by precipitation with both water and ethanol. One possible reason for this outcome is that the separation temperatures are so close to the melting point of BDMIM Cl, estimated to be 94-96 °C (sigmaaldrich.com). Although performing a dissolution at 90 °C, which is below the melting point reported by Sigma Aldrich, was difficult, the solution remained liquid, probably remaining in a super-cooled state due to stirring. Neither precipitate, when analyzed for the 110 °C and 8 h separation, was found to have any lignin. A small amount of cellulose, <5%, was found in both the water and the ethanol precipitates, with the remainder of >95% being hemicellulose or aqueous solubles. Since removing hemicellulose from biomass is less difficult than removing other biomass components (Lynam et al., 2011; Yan et al., 2009; Zhao et al., 2010), these findings are not particularly impressive. Although other solvents might give a different outcome, the difficulties in working with an IL of such high melting point would seem to outweigh any advantage, considering these unremarkable results.
4.3.1.4 Mass yield from AMIM Cl pretreatment precipitates

AMIM Cl dissolves approximately 15 wt% of the original rice hull mass for most of the run conditions except the 110 °C and 8 h separation, in which case about 30% of the mass was precipitated out (Fig. 4.3d). The data point for 90 °C, is inexplicably anomalous, and would have been repeated to insure accuracy if more AMIM Cl had been available. The longer duration, in this case, permitted more time for IL to diffuse into the silica covered rice hull structure, and for mostly hemicellulose to diffuse out. Neither precipitate, when analyzed for the 110 °C and 8 h separation, was found to have any lignin. A small amount of cellulose, <5%, was found in each of the water and the ethanol precipitates, with the remainder of >95% being hemicellulose or aqueous solubles. Unless a different precipitating agent is found which is more effective, this IL may be of little value in use with rice hulls.

4.3.2 Lignin removal by ionic liquids

The presence of lignin is one of the main reasons lignocellulosic biomass is so recalcitrant in processing. The removal of lignin has been suggested to correlate with the availability of cellulose for enzymatic hydrolysis (Kilpelainen et al., 2007; Lee et al., 2009). After dissolution of rice hulls in the four studied ILs at 90 °C or 110 °C for 4 or 8 h, a modified fiber analysis method (Goring and Van Soest, 1970) was used on the remaining pretreated rice hulls to determine what percentage of Klason lignin (acid insoluble) had been removed. Modified fiber analysis was carried out in triplicate on original rice hulls and gave values of 12% lignin, 39% cellulose, 16% hemicellulose, 12% aqueous solubles, with 21% ash determined by TGA and an ASTM method.
(Ehrman, T., 1994). The % lignin (or other components) removed is calculated as follows:  
\[
\% \text{lignin removed} = 100\% \times \frac{\text{original rice hull mass} \times \text{raw rice hull lignin fraction}}{\text{final sample mass} \times \text{pretreated rice hull lignin fraction}} / \frac{\text{original rice hull mass} \times \text{raw rice hull lignin fraction}}{\text{final sample mass} \times \text{pretreated rice hull lignin fraction}}.
\]

4.3.2.1 Lignin removal by EMIM Ac

As displayed in Fig. 4.4a, when rice hulls were solubilized by EMIM Ac, lignin was removed. Only a small amount was removed by the 90 °C runs. The 110 °C, 4 h run removed 46% of the lignin in the rice hull, while the 110 °C, 8 h runs removed all lignin according to the fiber analysis procedure. The 110 °C, 8 h dissolution in EMIM Ac was repeated to ensure accurate results, and in each case all lignin was found to be removed. A run at the same conditions with recycled EMIM Ac showed 80% lignin removal. The increase in solubilization temperature increases the diffusivity, both by adding energy to the system and by decreasing the ionic liquid’s viscosity (Sun et al., 2009). The additional time allows the EMIM Ac to penetrate farther into the rice hull, entering the silica covering through cracks produced by milling. The ability of EMIM Ac to remove lignin from rice hulls is remarkable.
Figure 4.4 Percentage of a) lignin and b) hemicellulose removed by EMIM Ac pretreatment from fiber analysis
Why is EMIM Ac so efficient in removing lignin? EMIM Ac has greater basicity than other ILs, such as AMIM Cl or 1-butyl-3-methylimidazolium chloride (BMIM Cl) (Sun et al., 2009), and thus it might be expected to be effective in disrupting inter and intramolecular hydrogen bonding in biopolymers. EMIM Ac’s lower melting point and viscosity, compared to Cl\(^{-}\) containing ILs, may also make it more successful in penetrating a biomass’s interior, especially for a silicon-shielded biomass such as rice hulls. Sun et al. (2009) in a 110 °C, 16 h pretreatment found a > 90% dissolution of southern yellow pine with EMIM Ac compared to approximately 50% when BMIM Cl was used. The acetate ion in EMIM Ac may also be particularly effective in removing the kind of lignin that exists in rice hulls, which is predominately guaiacyl and p-hydroxyphenyl.

4.3.2.2 Lignin removal by HMIM Cl

The short-coming of using fiber analysis on biomass show up when it is used on rice hulls pretreated with HMIM Cl. Under all dissolution conditions, it appears that extra lignin is generated by the pretreatment. These findings contradict the results of the precipitate analysis in section 4.3.1.2, in which some lignin was found in the water precipitate from the 110 °C, 8 h run. There are several possible explanations for the fiber analysis result. Guo et al. (2010a) have shown dramatic hydrogen bonding between cellulose and Cl\(^{-}\) ions. Such bonding may occur between the 3-dimesional network of lignin and HMIM Cl, entrapping the IL so that it is not removed by the 72 % sulfuric acid solution used to remove cellulose in the NDL-ADF-ADL method (Goering and Van
Soest, 1970). Thus, the HMIM Cl would show up as extra lignin. Another possibility is that the HMIM Cl acts as a catalyst to covalently bond other molecules existing in the lignocellulosic structure to lignin. No matter what the mechanism, the fact remains that little lignin can be removed from rice hulls using HMIM Cl with the precipitating agents tried, and the water precipitate is a mixture of cellulose and lignin. HMIM Cl appears to less useful in removing lignin than EMIM Ac.

4.3.2.3 Lignin removal by BDMIM Cl and AMIM Cl

Fiber analysis of the rice hull residue showed no lignin removal from rice hulls by BDMIM Cl, which agrees with the precipitate analysis in section 4.3.1.3. A replication of the 90 °C and 4 h dissolution with BDMIM Cl was performed to ensure accuracy, which gave the same result. AMIM Cl pretreatment also showed no lignin removal, as did its precipitate analysis in section 4.3.1.4. These two ILs are ineffective in dissolving lignin. Kilpelainen et al. (2007) suggested that AMIM Cl could not fully interact and solvate lignin because of lignin’s aromatic character.

4.3.3 Ionic liquid effect on cellulose in rice hulls

The effect of over 65 ionic liquids on cellulose has been investigated (Maki-Arvela et al., 2010). The separation of cellulose from lignocellulosic biomass without the use of hazardous chemicals or high temperatures/high pressures is a very desirable goal. Such cellulose can then be used to make polymers or can be fermented to make ethanol after enzymatic hydrolysis.
4.3.3.1 *EMIM Ac effect on cellulose in rice hulls*

As noted in section 4.3.2.2, rice hulls dissolved in EMIM Ac at 110 °C for 8 h are completely lignin-free. Fiber analysis of cellulose content after pretreatment was complicated by what may be EMIM Ac remaining in cellulose microfibrils, since their position there is a very low energy state (Guo et al., 2010b). Precipitate analysis (section 4.3.1.1) of the 110 °C and 8 h separation showed about 5% of the cellulose removed by water precipitation. Thus, much of the cellulose likely remains in the solid product of the dissolution. It is possible that this product could be enzymatically hydrolyzed to produce glucose prior to fermentation to biofuel. When Singh et al. (2009) dissolved switchgrass in EMIM Ac prior to regeneration, remaining remnants of the IL did not appear to inhibit subsequent enzymatic hydrolysis. Thus, dissolution of rice hulls in EMIM Ac at 110 °C for 8 h may be a useful pretreatment to isolate cellulose from lignin prior to further steps along the path to biofuel.

4.3.3.2 *HMIM Cl effect on cellulose in rice hulls*

Fiber analysis again appears to be problematic in determining cellulose removal from HMIM Cl pretreatment. It shows no cellulose removal, possibly because entrapped IL replaces dissolved cellulose. At the 110 °C and 8 h dissolution conditions, approximately 20% of the cellulose in the rice hull sample was precipitated out with water. This regenerated cellulose could be used to produce biofuels, as discussed in section 4.3.1.2.
4.3.3.3 **BDMIM Cl effect on cellulose in rice hulls**

Fiber analysis of the solid rice hull residue remaining after BDMIM Cl treatment showed no removal of cellulose in any of the 90 °C runs. A repeat of the 90 °C, 4 h dissolution still revealed no cellulose removal from the rice hull sample. However, fiber analysis of a 110 °C, 4 h dissolution gave a 10% cellulose removal and 110°C, 8 h showed 4% of the cellulose to be removed. These agree with the precipitates removed from the 110°C, 8 h run, which showed a small amount of cellulose (section 4.3.1.3). The higher temperature of 110°C, compared to 90°C, apparently increases diffusivity, especially by decreasing the viscosity of this high melting temperature IL. Thus, the BDMIM Cl is capable of penetrating the rice hull structure and some cellulose is able to diffuse out. In comparison, for dissolution of Avicel (pure cellulose), Kosan et al. (2008) reported 12% cellulose to be dissolved at 85 °C. The small amount of cellulose removed makes this IL less than promising for further study or use.

4.3.3.4 **AMIM Cl effect on cellulose in rice hulls**

Fig. 4.5 displays the percentage of cellulose removed by AMIM Cl at the various dissolution conditions as found from fiber analysis. A duplicate run at 110°C, 4 h yielded nearly exactly the same percentage of cellulose removed as the first run at that condition. The 110°C, 8 h dissolution exhibited a much higher cellulose removal than the others, with over 30% of the original cellulose being removed. Again, the increased thermal energy and decreased viscosity from a higher temperature increase diffusivity, while, in this case, a longer duration allows more AMIM Cl to enter and more cellulose to leave the rice hull. The 110 °C, 8 h run precipitates showed some cellulose (section 4.3.1.4),
but not this much. A different precipitating agent might have greater efficacy in removing dissolved cellulose from this IL. The large percentage of cellulose removed at the most severe conditions might justify searching for a better precipitating agent. In contrast, only 14.5% of cellulose pulp was able to be dissolved in AMIM Cl at 80 °C (Zhang et al., 2005). It appears that temperature and time are important parameters in the use of AMIM Cl with rice hulls.

Figure 4.5 Percentage of cellulose removed by AMIM Cl pretreatment from fiber analysis.

4.3.4 Hemicellulose removal by ionic liquid in rice hulls

Removing hemicellulose from biomass is a relatively simple process, requiring only hot water or dilute acetic acid at relatively low pressures (<2.6 MPa) and temperatures
(<230 °C) (Lynam et al., 2011; Yan et al., 2009; Zhao et al., 2010). Thus, using a presently expensive solvent to dissolve hemicellulose would be overkill. Nevertheless, it is interesting to see ionic liquids’ effects on rice hulls’ hemicellulose content as part of the overall scheme.

4.3.4.1 Hemicellulose removal by EMIM Ac in rice hulls

Fig. 4.4b shows fiber analysis results for the percentage of hemicellulose removed by EMIM Ac at different conditions. Little hemicellulose appears to be removed for the two 90 °C, 4 h runs. However, the 90 °C, 8 h run shows a much higher hemicellulose removal of over 60 wt%. This condition’s run showed only about 10 % lignin removal. It is possible that at the lower energy state of 90 °C, hemicellulose dissolution and diffusion out of the rice hull structure is possible, but the outward diffusion of highly cross-linked lignin is more difficult. The longer duration permits more of the hemicellulose to dissolve and diffuse out of the rice hull structure. At the higher temperature of 110 °C, the energy barrier for lignin dissolution may be reached, and it may be preferentially removed, compared to hemicellulose. In addition, at the 110 °C, 8 h condition, lignin may be broken down into pieces that are removed by the 1 M H₂SO₄ (ADF) fiber analysis treatment, but not the neutral fiber analysis (NDL), thus appearing to be additional hemicellulose. Curiosity about the actual mechanism of EMIM Ac dissolution of the rice hull structure prompted an SEM investigation into the pretreated products’ structure, as discussed in section 4.3.6.
4.3.4.2 **Hemicellulose removal by HMIM Cl in rice hulls**

Fiber analysis indicates that while no hemicellulose is removed by HMIM Cl by a 90 °C, 4 h dissolution, increasing duration to 8 h causes more than 50% of the hemicellulose to be removed at 90 °C. At the higher temperature of 110 °C for 8 h, over 70% of hemicellulose is removed. Again, the increase in solubilization temperature increases the diffusivity, both by adding energy to the system and by decreasing the ionic liquid’s viscosity, and additional time allows the HMIM Ac to penetrate farther into the rice hull. The analysis of precipitates for 110 °C, 8 h (section 4.3.1.2) indicated that only hemicellulose was precipitated by the addition of ethanol. Water did not precipitate hemicellulose. The estimated percentage of hemicellulose in the original rice hull sample that was precipitated out with ethanol was also over 60%, indicating the efficacy of this agent.

4.3.4.3 **Hemicellulose removal by BDMIM Cl and AMIM Cl in rice hulls**

Fiber analysis indicates that over 50% of hemicellulose is removed under 90 °C, 4 h conditions, and less (~30%) at other conditions by BDMIM Cl. Precipitate analysis (section 4.3.1.3) showed only hemicellulose to be precipitated by either water or ethanol. At all conditions except 110 °C, 8 h, fiber analysis showed that AMIM Cl removed somewhat over 50% of hemicellulose. At 110 °C, 8 h, approximately 75% of hemicellulose was removed.
4.3.5 Effect of ionic liquids on ash in pretreated rice hulls

For each pretreated rice hull sample, ash content was measured by TGA. Looking at Fig. 4.6, the percentage of ash removed by ionic liquid dissolution varies from 5% to nearly 60%. For EMIM Ac, approximately 10% is removed under all run conditions except 90 °C, 8 h, where 59% is removed. The 90 °C, 8 h condition for EMIM Ac dissolution is also that in which the greatest amount of hemicellulose is removed as determined by TGA. A 110 °C, 8 h run using recycled EMIM Ac showed an even higher hemicellulose % removal of 87% and gave a high ash removal of 33%. With HMIM Cl, 10-20% of ash is removed, with the 110 °C, 8 h condition showing the highest ash removal. Again, the highest ash removal appears to correlate with highest hemicellulose removal. In the BDMIM Cl runs, reproducibility is poor, but roughly 20% of ash is removed for all conditions. For AMIM Cl, ash removal is 15% under all conditions except 110 °C, 8 h, where is increased to 36%. Once more, the highest ash removal for AMIM Cl is associated with the highest hemicellulose removal (75%) as found by TGA.
%ash removed by EMIM Ac pretreatment

%ash removed by HMIM Cl pretreatment

a)
b)
Figure 4.6 Percentage of ash removed by a) EMIM Ac, b) HMIM Cl, c) BDMIM Cl, and d) AMIM Cl, from TGA.

The position of silica in the rice hull structure as it relates to lignocellulosic components has not been thoroughly studied. Zakharov et al. (1993) have suggested that
bonds exist between silicon and organic compounds and that silicon is present in the form of chemical compounds with starch and sugar. Silica sol or gel particles, of about 5 nm, are likely separated by organic layers, so that they are distributed in an organic matrix (Zakharov et al., 1993). The data presented in the preceding paragraph imply that a large amount of the silica particles in rice hulls are embedded in hemicellulose. Once hemicellulose is solubilized, the silica it contains apparently migrates into the ionic liquid. A separation scheme, perhaps using a centrifuge, might be able to remove the rice hull silica. Rice hull silica, since it has a finer particle size than quartz sand, could be a useful source for production of molecular sieves, catalyst supports (Bansai et al., 2006), photocatalysts (Artkla, 2009) and adsorbents to remove metal ions (Wang, 2008), as mentioned previously.

4.3.6 Scanning electron microscopy of raw and rice hulls pretreated with EMIM Ac

4.3.6.1 SEM comparison of outer rice hull before and after EMIM Ac

Fig. 4.7a-e shows scanning electron microscope (SEM) pictures at 600x magnification of the outer hull, the part which originally was furthest from the rice grain. Fig. 4.7a shows a raw rice hull’s outer surface. The protrusions which look like corn kernels on a corn cob are the outer hulls bristles. The blender processing, to reduce the hulls’ sizes to between 1.168 and 1.651 mm, likely broke off the tips of the bristles, making them look more rounded. This broken area would likely have less silica protecting the lignocellulosic material inside. The debris surrounding the raw rice hull bristles may be bristle tips or smaller mesh size rice hull pieces clinging to the larger mesh size. The SEM picture of Fig. 4.7b shows the outer hull surface after treatment in
EMIM Ac at 90 °C for 4 h. Nearly all debris is removed, as the IL would have had excellent access to the tiny pieces to solubilize them. In addition, some cracks are appearing to form on the structures’ tops, in contrast to the more rounded tops of the raw rice hull. These cracks likely formed because the breaking off of the bristle tips in mechanical processing exposed lignocellulosic material there unprotected by silica. Fig. 4.7c shows a rice hull after treatment in EMIM Ac at 90 °C for 8 h. All debris appears to have been dissolved by the IL. The quite round bristle structures of the raw and 90 °C for 4 h pretreated pictures is replaced a bicuspid shape. The gap between the protrusions appears to have increased. Two explanations exist for these observations. First, the IL may be dissolving the edges of the bristle base and the top and sides where cracks appeared for the treatment at 90 °C for 4 h. Thus, a figure 8 or a bicuspid tooth shape would form, and the bristle structures would appear to be more widely spaced. Secondly, as the IL dissolves the other side of the rice hull, making it less rigid, the entire hull could stretch, making the bristle farther apart. Looking at this picture carefully, stretch marks between the bristle structures can be noted.
Fig. 4.7 a) Raw rice hull outer surface b) 90°C, 4 h EMIM pretreatment, outer surface.
Fig. 4.7 c) 90°C, 8 h EMIM pretreatment, outer surface. d) 110°C, 4 h EMIM pretreatment, outer surface.
Fig. 4.7 e) 110 °C, 9 h pretreatment, outer surface, f) Raw rice hull, inner surface and edge
Fig. 4.7 g) 90 °C, 4 h pretreatment, inner surface and edge, h) 90 °C, 8 h pretreatment, inner surface and edge,
Fig. 4.7 i) 110 °C, 4 h pretreatment, inner surface and edge, j) 110 °C, 8 h pretreatment, inner surface and edge.
Fig. 4.7 k) Typical amorphous structure after 110 °C, 8 h pretreatment at x300 magnification.

Fig. 4.7 a-k SEM comparison of rice hulls before and after EMIM Ac treatments (at x600 magnification, except k) which is 300x magnification.) a) Raw rice hull outer surface, b) 90 °C, 4 h pretreatment, outer surface, c) 90 °C, 8 h pretreatment, outer surface, d) 110 °C, 4 h pretreatment, outer surface, g) 90 °C, 4 h pretreatment, inner surface and edge, h) 90 °C, 8 h pretreatment, inner surface and edge, k) Typical amorphous structure after 110 °C, 8 h pretreatment at x300 magnification.
Looking at the SEM picture of a rice hull’s bristled side after treatment in EMIM Ac at 110 °C for 4 h (Fig. 4.7d), large transverse cracks appear to have split the bristle structures, such that spaces no longer appear between them. The higher processing temperature must have increased the IL’s diffusivity to such an extent that, where the bristle tips were broken, the IL could penetrate and dissolve the lignin holding the sides of the bristle together. When the pretreatment time was increased to 8 h at 110 °C, very little structure remains as illustrated in Fig. 4.7e. The solid remaining after treatment seems jelly-like, with a very small proportion of distinguishable rice hull embedded. It is difficult to see structure that may be outer rice hull. Lignin is notorious for self-condensation reactions. If any cleavage reactions occur during dissolution, repolymerization may occur, which may change the form of the biomass (Binder et al., 2009). In Fig. 4.7e, the 110 °C, 8 h SEM picture, some bristle structures appear to have merged, while others seem to have been completely reacted. An extra experiment was performed in which the rice hulls were stirred in EMIM Ac at 110 °C for 24 h. The result of this pretreatment was completely jelly-like, with no remaining discernable rice hull.

4.3.6.2 SEM comparison of inner rice hull surface and edge before and after EMIM Ac pretreatment

Fig. 4.7f-k shows SEM pictures at 600x magnification of the inner hull surface, the part which originally was closest to the rice grain, and the edge between the inner and outer surfaces. For Fig. 4.7f, of raw rice hull, the inner silicon “armor” is mostly smooth, with some cracks and debris from the mechanical blender treatment. A “peeling paint” appearance at the edge again reflects the milling process. Fig. 4.7g shows an SEM picture
of a rice hull’s inner surface and edge after treatment in EMIM Ac at 90 °C for 4 h. Again, the debris is removed by the IL, and the inner hull surface is even smoother, but with smooth pits likely due to incursions of the IL where initial cracks occurred. The edge itself has a honeycomb structure, perhaps because pores are evenly exposed. The Fig. 4.7h SEM picture shows a rice hull after treatment in EMIM Ac at 90 °C for 8 h. A trench between the inner and outer hull surfaces has appeared, perhaps because this area, unprotected by silica, has been solubilized by the IL. Also, it is likely that the cover of silica on the now less smooth inner hull surface exposes the partially dissolved structure underneath, like a person under his sheets. Stretch marks again appear at this particular temperature and time pretreatment. This appearance may relate to the higher removal of hemicellulose, since more of it was removed under these particular conditions. The lower dissolution temperature may not allow EMIM Ac to dissolve much lignin, as discussed in section 4.3.2.1.

The SEM picture of a rice hull’s inner side and edge after treatment in EMIM Ac at 110 °C for 4 h (Fig. 4.7i) displays what appears to be a deeper trench. The silica cover on the inner surface, if it exists, allows a good view of vascular bundles emerging. The higher temperature has permitted the IL to diffuse deeper in the hull structure, dissolving it even more, especially the lignin. When the EMIM Ac was permitted to solubilize the rice hulls at 110 °C for 8 h, very little structure remained, as shown in the Fig. 4.7j SEM picture. Pieces of what might be the inner silica cover are gone. The removal of lignin and hemicellulose from the biomass has apparently caused the remaining cellulose to become quite amorphous. Amorphous cellulose, with its higher surface area is quite
available to enzymatic hydrolysis compared to crystalline cellulose or biomass (Lee et al., 2009; Li et al., 2010; Singh et al., 2009; Zhao et al., 2009; Zhao et al., 2010). The Fig. 4.7k SEM picture shows what rice hulls typically look like after an EMIM Ac at 110 °C for 8 h pretreatment at a x300 magnification. This image is quite similar to one that Singh et al (2009) reported after regeneration of cellulose using water, when switchgrass was dissolved in EMIM Ac at 120 °C for 3 h. It is also similar to an SEM picture reported by Sun et al. (2009) for southern yellow pine after a 16 h EMIM Ac treatment at 110 °C. Since cellulose does not appear to be extensively removed by this treatment for rice hulls, while lignin and hemicellulose are, it is possible that cellulose may be made quite available for further use by this pretreatment. The ability of this IL to pierce the silica armor of rice hulls is quite remarkable.

4.4. Conclusions

Rice hulls, when dissolved in EMIM Ac at 110°C for 8 h, have all their lignin removed, according to fiber analysis, and are almost completely amorphous as seen in SEM pictures. This solid product, consisting of mostly cellulose, could be enzymatically hydrolyzed prior to fermentation to produce biofuels, as could the cellulose-rich precipitate created from adding water to the used EMIM Ac. A possibly useful lignin-rich precipitate was produced by ethanol addition to the used EMIM Ac. EMIM Ac displays interesting and valuable properties when used to dissolve rice hulls.
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4.5 References


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Chapter 5

Conclusions and Recommendations for Future Research

5.1 Conclusions

5.1.1 Hydrothermal Carbonization: Acetic Acid and LiCl Addition

Performing hydrothermal carbonization (HTC), also known as wet torrefaction, on loblolly pine at 230°C reduces the mass of the original biomass for lower cost transportation and enhances higher heating value (HHV). Addition of acetic acid and/or lithium chloride to this process can increase the HHV and reduce mass yield even further. Lower mass yield reduces transportation costs. Higher energy densification means that little energy yield loss results. Cellulose degradation is promoted by the addition of acetic acid and/or LiCl.

In large-scale HTC, addition of lithium chloride to the reactor would require that the reactor have a glass lining to prevent pitting of the underlying metal, adding to the fixed cost of the reactor. In addition, the LiCl would have to be purchased for addition to the process, although it could be recycled to treat fresh batches. Its reduction of pressure in the reactor enhances the safety of the process and it increases energy densification more than acetic acid addition. If both 0.4 g of acetic acid and 1 g of LiCl per g of loblolly pine are added to the hydrothermal carbonization process at 230°C, HHV is similar to and mass yield is lower than that produced at 260°C. Thus, less heating and lower pressure would be required in the process.
Since acetic acid is produced by the process, it could be recycled for use, reducing or eliminating the cost of addition. The optimal level is 0.4 g of acetic acid per g of loblolly pine, a level at which no further acetic acid is produced. Acetic acid may be valuable as an additive in hydrothermal carbonization of biomass.

5.1.2 Salt Addition Effect on Hydrothermal Carbonization

If lignocellulosic biomass, a renewable, non-food energy resource, is co-fired with coal, the quantity of fossil fuel required for electricity production is reduced. The low energy density disadvantage of lignocellulosic biomass can be ameliorated by pretreating the biomass using hydrothermal carbonization. If salts are added to this high pressure process, reaction pressure can be reduced and energy density can be increased, compared to the process without additives. Adding Ca lactate, Li chloride, and Ca chloride to the hydrothermal carbonization pretreatment of loblolly pine enhanced the reactions occurring so that the resulting biochar had increased HHV compared to that with no salt added. Adding Ca salts has been shown by others to reduce SO\textsubscript{x} and NO\textsubscript{x} emissions from coal thermal conversion processes, so that they are of particular value. Inexpensive calcium chloride showed a particularly high energy yield and a large reduction in hydrothermal carbonization pressure. If a Ca salt without chloride is desired, calcium lactate showed a high energy densification and some pressure reduction when added to the hydrothermal carbonization process.
5.1.3 Ionic Liquids Effect on Rice Hulls

Of the ionic liquids 1-ethyl-3-methylimidazolium acetate (EMIM Ac), 1-hexyl-3-methylimidazolium chloride, (HMIM Cl), 1-butyl-2,3-dimethylimidazolium chloride (BDMIM Cl), and 1-allyl-3-methylimidazolium chloride (AMIM Cl), which have been suggested to be effective in dissolving biomass, only EMIM Ac and HMIM Cl were found to be of practical use when used to dissolve rice hulls. After running experiments at 90°C for 4 or 8 h, EMIM Ac at 110°C for 8 h was found to completely remove lignin from rice hulls, while ethanol, a safe anti-solvent, was capable of precipitating lignin out of the EMIM Ac. EMIM Ac thus has promise in removing lignin from rice hulls, so that the amorphous cellulose-rich residue should be amenable to enzymatic hydrolysis to produce bio-ethanol. In addition, HMIM Cl, when used at 110°C for 8 h on rice hulls, was found to precipitate out 20% of the original cellulose, which could be used for bio-ethanol or renewable polymer production. Another intriguing result is that ionic liquid removal of rice hull ash, an effective heavy metal adsorbent, appears to correlate with hemicellulose removal for all four ionic liquids.

5.2 Recommendations for Future Research

Salt and acetic acid additives to the hydrothermal carbonization process were only used on the model lignocellulosic biomass loblolly pine. A plethora of other biomass types with varying availabilities and properties exist which could be investigated for their use in energy generation. Also, with these additives, the focus was on a single temperature in each case, which could be varied to determine optimal conditions, even using a two step reaction temperature program to optimize product properties. Particle
size of biomass in hydrothermal carbonization has not been thoroughly investigated, nor has the effect of salt or acetic acid additives on pelletization of hydrothermal carbonization’s solid product.

Only four ionic liquids were investigated for use on the high volume secondary agricultural residue rice hulls, but many other possibilities exist, including ILs which use formate ions instead of acetate or chloride ions. Also, procedures for recycling of ionic liquids in biomass dissolution need to be investigated fully. Adding glycol or acids to the process may enhance them. In addition, if cellulose-rich material is obtained from an ionic liquid dissolution and re-precipitation with an anti-solvent, enzymatic hydrolysis, a “green” process can be performed to obtain glucose. Determining if such pretreatment makes a biomass or its cellulose precipitate more or less available for conversion to glucose is essential finding the proper direction for further biofuels research.