The production of fatty acid methyl esters in Lewis acidic ionic liquids

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The Production of Fatty Acid Methyl Esters
in Lewis Acidic Ionic Liquids

by

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Biodiesel is a direct substitute for petroleum derived fuels and can be utilized in diesel equipment with few or no modification (Ma, Hanna, 1999). Traditional sources for biodiesel include plant oils (such as soybean or canola) that are also important food sources; biodiesel derived from plants might therefore not result in substantial displacement of petroleum feedstocks. Algae may present itself as an alternate feedstock for biodiesel production that does not compete with the vital land and water resources needed for traditional agriculture. However, the production of fuels from algae is currently economically unviable due to several technological hurdles, including availability of efficient methods of converting cellular lipids to biodiesel.

The research described herein describes the in-situ transesterification of soy flour triglycerides (surrogate for algal biomass) with methanol to fatty acid methyl esters using a novel ionic liquid (IL) comprised of 1-Ethyl-3-methylimidazolium chloride (EMIMCl) and the metal halide AlCl$_3$. This IL exhibits Lewis acidity and has been shown to be an excellent nonvolatile solvent and catalyst for many chemical reactions including acylations, condensations, esterifications, and polymerizations. However, it is now proposed that this IL catalyst is able to perform esterification reactions with the addition of an organic solvent that solubilizes the ionic liquid yet allows it to retain its catalytic properties. This method enables the reaction to experience the benefits
of homogeneous catalysis while providing an opportunity for catalyst recovery and reuse.

The influences of biomass concentration, catalyst volume, organic solvent/methanol ratios, reaction time, and temperature on the generation of the desired reaction products has been studied. A traditional mechanistic pathway to account for the observed production of fatty acid methyl esters is proposed and the triglyceride carbon mass balance is closed. The sustained catalytic ability of the ionic liquid was explored and the importance of ionic liquid recovery and reuse will be discussed. In addition, preliminary findings regarding the production of acrylates from biomass and Lewis acidic ionic liquids will be presented.
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List of Abbreviations

AlCl$_3$ .................. Aluminum Trichloride

CHCl$_3$ ............... Chloroform

DCM ..................... Dichloromethane

EMIMCl ............... 1-ethyl-3-methylimidazolium chloride
EtOAc ............... Ethyl Acetate

FAME .................. Fatty Acid Methyl Ester

IL ...................... Ionic Liquid

MeOH .................. Methanol

NMR .................... Nuclear Magnetic Resonance

TGA ..................... Thermogravimetric Analysis
Chapter 1

Overview: Characteristics of Ionic Liquids

1.1 Introduction

In recent years, that has been an increased emphasis towards the development of environmentally sustainable technologies, particularly with regards to reducing our carbon footprint and reliance on non-renewable fossil fuels. With reports that oil peaking will occur within the next 15-30 years, it is important to explore the use of other sources for the production of fuel and substitutes for petroleum based products (Hirsch, Bezdek, Wendling, 2006). One potential renewable fuel source could be photosynthetically derived lipids (from oil seeds or algae) that can be converted into biodiesel through transesterification with simple alcohols (such as methanol, ethanol or butanol). Although biodiesel production from vegetable oils is commercially practiced, current industrial processes for fuel production from vegetable oils are not directly applicable to algae due to the inability to recover oil from algal biomass through simple mechanical pressing. Consequently, alternate algae-specific fuel production processes must be developed.
In accord with the theme of sustainable energy comes the idea of green technology. Green technology, a now common term, simply means that the process, regardless of its industrial genre, does not release emissions that are believed to be harmful to the environment. The increased interest in the use of molten salts, more commonly known as ionic liquids (ILs), can be attributed to the fact that these compounds have no measurable vapor pressure and also offer unique solvent and catalyst properties. In some manufacturing processes, ILs may be able to supplant toxic, flammable organic solvents, reduce the production of chemical waste, and eventually improve the safety of consumer products as well as industrial processes (Patell et al., 2002).

1.2 Characteristics of ILs

1.2.1 Composition and Properties

Ionic liquids are typically composed of a large asymmetric organic cation and an inorganic or organic anion with a protected negative charge (Kirchner, 2009). It is important to note that while these compounds may actually be solid at room temperature, they are typically referred to as liquids because they have a melting point below 100°C. The majority of the ionic liquids produced today are based on alkyl-substituted pyridinium and imidazolium cations, with halide or trihalogenoaluminate anions (Freemantle, 2010). Ionic liquids exhibit high thermal stability, which is often influenced by the nucleophilicity of the anion due to its role in the degradation of the cation. This means that certain anions, particularly metal halides, have a significant impact on the stability and measured melting points of the primary cation (Scammells, Scott, Singer; 2005). Since ILs remain molten over a wide temperature range, precise thermal and kinetic control of processes, including temperature dependent reactions or separation methods such as precipitation or crystallization, can also be carried out in ILs (Rogers, Brennecke, Seddon, 2007).
In addition, the physical and chemical properties of ILs can be easily adjusted by changing the cation and/or anion, altering the imidazolium and halogenoaluminate ratios, or by mixing two or more simple ionic liquids. Thus, ILs can be tailored to exhibit specific polarity, hydrophobicity, conductivity, solubility, melting point, viscosity and acidity, as well as many other properties (Freemantle, 2010).

1.2.2 Solubility and Miscibility

Ionic liquids exhibit a broad range of solubility and miscibility characteristics. Ionic liquids dissolve many polar organic compounds, metal catalysts, and gases, which then enables them to perform homogeneously catalyzed reactions. In addition, they are able to dissolve covalent and ionic compounds, making them ideal solvents for chemical processes and extractions (Dyson, Geldbach, 2005).

The miscibility of ionic liquids in water depends of course upon whether the IL is hydrophilic or hydrophobic. However, the coordinating ability of the anion is the primary determinant of an ionic liquids miscibility with water. Basic anions are strongly coordinating, while acidic anions are noncoordinating. In fact, as the anion becomes less coordinating, the hydrophilicity of the ionic liquid increases. The particular cation may also impact the hydrophilicity of ionic liquids, as it has been found that as the length of the alkyl chain on the cation increases, the respective IL becomes decreasingly miscible with water (Freemantle, 2010). When considering a broad reaching generalization, it can be said that ILs tend to be miscible with liquids consisting of polar molecules that have medium to high dielectric constants. However, ionic liquids are immiscible with many organic solvents and compounds. Thus, ionic liquids may also be an ideal media for biphasic reactions. Ideally, when considering biphasic reactions performed in ionic liquids, a soluble polar substrate would be converted to a less polar (and thus less soluble) product, which would then form a separate phase (Freemantle, 2010).
1.2.3 Impurities

The most common and problematic impurity in ionic liquids is water. Many ionic liquids are hygroscopic and need to be properly dried, particularly when utilized in water sensitive applications. Interestingly, it has been shown that even water-immiscible salts can absorb water when exposed to air. Fortunately, placing them under vacuum for several hours can properly dry the majority of the ionic liquids produced today (Rogers, Brennecke, Seddon, 2007). It must be mentioned however, that because ionic liquids bond strongly with water, vacuuming the sample alone may not be sufficient to achieve an acceptably low degree of water contamination. In such cases, it has been found that heating the ionic liquid to at least 70°C under vacuum for several hours with stirring can be advantageous (Wasserscheid, Welton; 2008). The IL of interest in this research, [EMIM]Cl (1-ethyl-3-methylimidazolium chloride), is a solid at room temperature and can be purified through a simple recrystallization (Freemantle, 2010).

Past studies have suggested that even the slightest impurities can have a profound effect on ionic liquid applications. For example, the density and viscosity can be radically altered by the presence of unwanted ions (Patell et al., 2002). Therefore, it is important to perform a proper analysis of the purity of any ionic liquid, particularly those that are synthesized at lab-scale. The structure and purity of an ionic liquid can be confirmed using nuclear magnetic resonance (NMR), and other various spectral techniques.

Lastly, impurities present in ILs may not only impact the IL itself, but may also result in deactivation of the catalyst. Many ionic liquid based catalytic systems are extremely sensitive to water, halide, and imine impurities, which may impact the ability of the catalytic ability of the catalyst (Stark et al., 2006).
1.2.4 Toxicity

Ionic liquids cannot be justified as green technology due solely to the fact that they are non-volatile. The level of persistence and degradability are two key factors that must be studied further in order to accurately determine the environmental friendliness of ILs (Rogers, Brennecke, Seddon; 2007). Although ionic liquids pose little to no risk of release into the air due to their low vapor pressures, they exhibit concerning levels of aquatic toxicity. Ionic liquids may be released into waste water, and thus, potentially into rivers, ground water, soil, and into the homes of the public. Sorption studies show that many ionic liquids exhibit a strong affinity for being held within soil and other sedimentary matter. This means that ionic liquids would likely transfer from water and become bound to any ground matter with which they come into contact, therefore reducing the likelihood of ground-water contamination (Crostwaite et al., 2005). Unfortunately, at this point, little is understood about the ability of an IL to spread through the environment once it has been released.

The aquatic toxicity of many ionic liquids has been studied in recent years. The lethal concentration (LC$_{50}$) values to marine organisms and fish for the majority of ILs used today are extremely low. In fact, LC$_{50}$ values for numerous ILs have been found to be significantly lower than those reported for organic molecular solvents (Pretti, 2006). Additionally, 1-alkyl-3-methylimidazolium ionic liquids have been studied in regards to their toxicity upon plants and mammals. It has been demonstrated that even low concentrations of these ILs exhibit acute toxicity to rabbits, mice, and rats and drastically inhibit plant growth (Jastorff et al., 2003). Because ILs are lipophilic and are able to interact with biological and environmental barriers, it has been suggested that the primary means of toxicity is through the disruption of the biological membrane, which becomes more severe with increasing length of the alkyl side chain (Rogers, Brennecke, Seddon; 2007).

The overall toxicity of ILs can be characterized by what is known as the "...
length effect.” This generalization has been formed from research that shows the toxicity of ILs increases uniformly with increasing alkyl chain length. However, as the chain length increases, ILs becomes less soluble in water, which may serve to inhibit their ability to spread through the environment and therefore decrease their potential for bioaccumulation (Jastorff et al., 2003). Currently, the most accurate way to measure the potential bioaccumulation of an IL is to investigate its partitioning between octanol and water. It has been shown that even hydrophobic ILs prefer water over octanol, and as such, their bioaccumulation potential is thought to be fairly low (Crostwaite et al., 2005). Nevertheless, it is evident that ILs need to be properly disposed of and further studied to ensure that all risk factors related to their use are properly accounted for before they become widely used in industrial applications.

1.3 Ionic Liquids as Catalysts

The development of aqueous-organic biphasic catalysis has been extremely beneficial in many aspects of scientific research and industry particularly with regard to catalyst and product recovery. Not only has it reduced the environmental impact of many processes, it also aids in preventing the loss of the catalyst. However, alternatives to water for biphasic catalysis are needed for numerous reasons, mainly poor solubility with organic compounds and catalysts. It is believed that ILs may be a suitable media to replace water in aqueous-organic systems because the hydrophilicity of an ionic liquid can be used in tandem with appropriate organic solvents to create multiphasic reactions (Kirchner, 2009).

In addition to being good solvents, ionic liquids have been shown to act as catalysts. They may also be used for separations and extractions due to the fact that they can be tailored to meet the needs of the respective organic solvent utilized (Freamantle, 2010). This dual functionality as both a solvent and catalyst imparted upon
ILs as a result of the fact that they consist of both cations and anions is a strategic characteristic that should be exploited in chemical processes. For example, many researchers have sought to develop ILs that are immiscible with reactants and products yet are able to dissolve compounds such as transition metal complexes that impart catalytic activity. This would technically be considered a homogeneous system due to the fact that the catalyst is dissolved in the same system in which the reaction takes place. Nevertheless, a system such as this would create a desirable catalytic process that is able to utilize the beneficial characteristics of both heterogeneous and homogeneous catalysis systems (Dyson, Geldbach, 2005).

Many ionic liquids are non-nucleophilic, thereby making solvated catalytic intermediates unlikely to form. This also makes ionic liquids less likely to deactivate a catalyst and may then lead to increased turnover numbers, which are needed in biphasic catalysis where catalyst reuse is desired (Freemantle, 2010; Dyson, Geldbach, 2005). Lastly, the active catalytic species may be generated in situ from the metal salts that are incorporated into the IL where the IL itself may act as both solvent and catalyst.

1.3.1 Application of ILs in Organic Reactions

To date, ILs have been used for a number of reactions including, electrophilic substitutions, condensation reactions, dimerizations, and cycloadditions (Rogers, Brennecke, Seddon, 2007). In fact, ionic liquids have been utilized in electrochemistry, materials science, pharmaceuticals, and biochemistry.

Surette and Singer found that ionic liquids allow for the formation of new carbon-carbon bonds in organometallic compounds (1996). For example, acidic chloroaluminate ionic liquids can act as solvents and their [Al₂Cl₇]⁻ anions as Lewis acid catalysts for Friedel-Crafts alkylation and acylation. While imidazolium chloroaluminate ionic liquids have typically been used for Friedel-Crafts alkylation, they are
also gaining interest as dual function media for cracking reactions. EMIMCl-AlCl₃ has been used to crack polyethylene with the addition of an acidic co-catalyst. The products were a mixture of gaseous alkanes and cyclic alkanes with low volatility in yields above 90 percent. Additionally, the side production of aromatic hydrocarbons and olefins was minimal when compared to traditional processes and the products were readily separated from the IL, allowing it to be efficiently recycled (Adams, Earle, Seddon). Because ionic liquids have been demonstrated to serve as effective media for a number of organic transformations, only a few of the pertinent reactions involving chloroaluminate ILs will be discussed here.

1.3.2 Metathesis

Lewis acidic chloroaluminate ionic liquids have been used in the transposition of carbon-carbon double bonds in alkenes in an organic reaction known as olefin metathesis. This is an important reaction used for the production of fuels, medicines, and polymers with the added advantage of fewer byproducts and wastes. The metathesis reactions are known as cross and self-cross metathesis. In cross metathesis, the double bond of an alkene is redistributed through the scission of the double bond in another alkene, resulting in the formation of two new alkenes. In comparison, self-cross metathesis occurs when two identical alkenes react to form one or more new alkenes (Freemantle, 2010. Dyson, Geldbach; 2005). The conventional methods of olefin metathesis suffer from the fact that high catalyst loadings are required for acceptable reaction rates. Additionally, the commonly used ruthenium-based catalysts are not easily separated from the product, which are often polymers. Recently, ionic liquids have been thought to be a potential solution to these and other problems related to homogeneous olefin metathesis. In fact, metathesis reactions can be carried out in ionic liquids with relative ease and significant rates of reaction, even when compared to traditional molecular solvents.
1.3.3 Polymerization

The catalysts utilized in polymerization reactions are poorly soluble in traditional organic solvents. In addition, the catalyst residue that results from these reactions is difficult to separate from the polymer product. Chloroaluminate ionic liquids are useful for polymerization processes, where higher rates of polymer propagation with lower rates for termination are observed. For example, ILs have been used to carry out the oxidative polymerization of benzene to polyphenylenes. The resulting polymers had molecular masses higher than those formed in traditional solvents due to the fact that the polymers were more soluble in the IL, which aided the polymerization (Kobryanskii, Arnautov; 1992). Traditional Ziegler-Natta catalysts have also been used to polymerize ethylene in acidic chloroaluminate systems with much success (Carlin, Osteryoung; 1990). It should also be noted that living polymerizations may be performed in ILs. These polymerizations are unique because they do not have a termination reaction and/or the rate of chain growth is much faster than that of termination. However, these reactions are able to produce highly controlled products and are governed by the addition of a simple monomer (Dyson, Geldbach; 2005).

1.3.3.1 Dimerization and Oligomerization

The dimerization and oligomerization of linear alkenes to other oligomers such as dimers has been studied in chloroaluminate ionic liquids. These reactions result in the synthesis of linear and branched olefin dimers, of which various isomers may be present. For example, Chauvin, Gilbert, and Guibard demonstrated that the dimerizations of alkenes could be carried out using nickel complexes dissolved in acidic chloroaluminate ionic liquids (1990). In almost all scenarios, it has been found that the oligomerization proceeds with better reactivity and selectivity for the products than when carried out in conventional solvents (Wasserscheid et al., 2001). In addition, olefins, including acrylates, can be catalytically dimerized using chloroaluminate
1.3.4 Alkylation and acylation

Chloroaluminate ionic liquids, particularly those with imidazolium cations, have been utilized for alkylations using electrophilic alkylating agents. Lewis acidic binary mixtures of EMIMCl and AlCl$_3$ are used with alkyl halides (the alkylating agent) to perform Friedel-Crafts alkylations and acylations. In these reactions, a hydrogen atom on an aromatic ring is replaced with an alkyl or acyl group (from an alkyl or acetyl halide) as part of an electrophilic substitution. Lewis acidic aluminum chloride is typically dissolved in a solvent and used as a catalyst for this reaction. Boon et al., found that acidic [EMIM]Cl-AlCl$_3$ acts as both the catalyst and solvent for the alkylation and acylation of benzene (1986). In addition to using alkyl halides for alkylation aromatic compounds, olefins may be used to produce linear hydrocarbons through a similar mechanism (Abdul-Sada et al., 1995).

It has also been found that acidic [EMIM]Cl-AlCl$_3$ is able to conduct acylations of aromatic hydrocarbons, ethers, and halides with yields and selectivities comparable to those achieved in conventional solvents (Adams et al., 1998). In comparison to organic solvents, acidic chloroaluminates offer several advantages for Friedel-Crafts aromatic substitution reactions. For example, product separation is simplified, the catalyst can be recovered and reused, and the substituted product is synthesized with higher selectivity. Acylations are also used to synthesize aromatic ketones, which are important intermediates in the production of dyes, pharmaceuticals, and agrochemicals.
1.4 Biomass Conversion

Imidazolium ionic liquids are suitable media for the acid-catalyzed hydrolysis of lignocellulosic materials into glucose, xylose, and other saccharides (Kirchner, 2009. Li, Wang, Zhao; 2008). ILs are known to solubilize cellulose and hemicellulose in lignocellulosic materials, which facilitates easy conversion of these biopolymers into fuels/products through subsequent action of chemical catalysts or enzymes. In fact, chloroaluminate ILs are even capable of dissolving highly recalcitrant polymers such as kerogen, which had been found to be insoluble in all known solvents with the exception of hydrofluoric acid (Patell et al., 2002).

Swatlowski et al., reported that imidazolium chloride ionic liquids are capable of dissolving cellulose pulp (2002). The mechanism for this solubility is thought to result from the disruption of the cellulose hydrogen-bonding network and the subsequent formation of hydrogen bonds between the chloride anions and the hydroxyl groups of the cellulose. The acetylation of cellulose has been carried out effectively in [EMIM]Cl alone without the need of an acidic metal halide. The resulting product, cellulose acetate, had a controllable degree of substitution and yields of up to 86 percent have been obtained via reactions at 80°C for 2 hours (Kirchner, 2009). In addition, ILs are able to partially dissolve woods such as pine, poplar, oak, and eucalyptus (Freemantle, 2010; Rogers, Brennecke, Seddon, 2007; Earle, Seddon, 2000).

From the literature presented above, it is easy to hypothesize that the free fatty acids of other simple types of biomass, particularly soy flour and algae, can be easily extracted using these ionic liquids. The dissolution of soy flour is believed to be based upon the same mechanism as cellulose dissolution. This would then require the complete absence of water, which necessitates drying of the biomass, small particle size, drying of the IL, and reaction under an inter atmosphere (Lui et al., 2007).
1.4.1 Transesterification using ILs

The ability of ILs to solubilize triglycerides is a critical factor in the reaction rate of IL-based systems (Chen et al., 2008). ILs may be capable of creating an effective interaction of immiscible substrates, therefore reducing mass transfer limitations (Prabhavathi Devi, Guo, Xu, 2011). As a result, it is believed that ILs may be able to displace common alkaline catalysts used in the production of biodiesel from biomass and vegetable oils (Cooney, Young, 2009).

The use of ILs as a reaction media for the biocatalytic production of biodiesel from plant biomass has been explored by a number of groups. De Diego et al., found that imidazolium ILs provide for biodiesel production while allowing for the selective extraction of products in a three-phase system that offers recycling of the IL and catalyst (2011). In another study, it was found that biodiesel and glycerol automatically partition when using IL catalysts and the reaction equilibrium favors maximum yield of biodiesel without the accumulation of intermediate products (Prabhavathi Devi, Guo, Xu, 2011). The small amount of IL needed, catalyst recovery, product separation and the protective effect it imparts upon biocatalysts make ILs an attractive alternative to traditional alkaline and acidic catalysts (De Diego, 2011, Prabhavathi Devi, Guo, Xu, 2011).

1.5 Summary

The structure of both the cation and anion play a very important role in the properties of all ionic liquids. Even minor and seemingly insignificant modifications to either of the ions can cause a significant change in any and all properties of the ILs, making them highly customizable to specific applications.

Ionic liquids are thought to be more attractive than water and conventional organic solvents as media for catalysis. The rates of reaction and selectivity imparted upon a
particular chemical reaction through the use on an IL are usually better than those found in molecular solvents. Because ILs may be the next revolution in catalysis, it is important to consider product and catalyst recovery. Thermally stable volatile organic reaction products can be readily separated from the ionic liquid media under vacuum or by distillation without the formation of an azeotrope. However, this may not be possible in cases where the products are highly reactive or temperature sensitive. It should also be noted that it is possible to remove volatile compounds by stripping the IL with an inert gas or vapor.

Despite their advantageous properties, ionic liquids suffer from issues related to toxicity, cost, corrosiveness, recyclability, and final disposal, which must be studied before they are used widely in industrial applications (Wasserscheid, 2003). Nevertheless, the utilization of ionic liquids is an important step towards the development of industrial processes that are environmentally benign.

Although ILs containing chloroaluminate anions show good catalytic properites, large scale applications involving these ILs would have to carefully consider the implications of their relatively high sensitivity to moisture and air. In addition, water-miscible ionic liquids are difficult to recycle as inorganic by-products can not be easily removed and they may suffer from degradation resulting from the extraction of certain organic products (Wasserscheid, 2008).

It is obvious that ionic liquids, particularly those containing imidazolium chloride are gaining momentum as media for biomass based processes. However, issues related to biomass heterogeneity that result in a wide variety if decomposition products remain to be addressed (Liu, 2007). Ultimately, issues related to product recovery and separation, ionic liquid recycling and toxicity need to be further studied as they are vital to the economic viability of any relevant industrial application involving ionic liquids.
Chapter 2

Imidazolium Based Ionic Liquids

2.1 Introduction

The imidazolium cation is a five-membered heterocyclic cation with a positively charged nitrogen center (Welton, 1999). The common anions associated with ionic liquids based on the imidazolium cation are nitrates, chloroaluminates, hexafluorophosphates, tetrafluoroborates, alkyl sulfates, and the halides bromide and chloride (Freemantle, 2010. Rogers, Brennecke, Seddon, 2007).

The majority of imidazolium based ionic liquids are prepared by the alkylation of the nucleophilic ion by a halogenoalkane. In the case of 1-ethyl-3-methylimidazolium chloride (EMIMCl), the synthesis involves fusion of the 1-methylimidazole ring with gaseous chloroethane. The synthesis scheme can be seen in Figure 2-1 (Wasserscheid, 2008. Dyson, Geldbach, 2005). The production of [EMIM]Cl is generally carried out in an autoclave, with the chloroethane cooled to below its boiling point before being added to the reaction mixture. The products are collected at high temperature, as this halide salt is a solid at room temperature. The most important requirement is that the reaction mixture be kept free of moisture, as the products are extremely hygroscopic and the halide salt products are typically immiscible in the starting ma-
terials (Stark et al., 2006). The newly formed EMIMCl ionic liquid has a melting point of 87°C and thus maintains a crystalline structure at room temperature. These imidazolium based ionic liquids are particularly reactive due to the presence of the acidic proton at the 2-position of the ring (Freemantle, 2010).

![Synthesis of EMIMCl](image)

Figure 2-1: Synthesis of EMIMCl

### 2.2 Binary Mixtures

The majority of ILs of interest today are binary mixtures of an organic and inorganic salt. The IL used in this work is a binary mixture of EMIMCl, the organic salt, and aluminum chloride, the inorganic salt. The newly formed binary ionic liquid, denoted as EMIMCl-AlCl$_3$ will be referred to throughout this thesis as ”chloroaluminate”. The primary advantage of synthesizing a binary haloaluminate IL is the ability to adjust its Lewis acidity by varying the molar ratio of the organic salt and metal halide.

The ratio of cation to anion in chlorometallate ionic liquids impacts both the physical properties and the chemical behavior of the resulting binary mixture. This type of ionic liquid is synthesized from the direct reaction of the solid [cation]Cl and a metal chloride (Welton, 1999. Dyson, Geldbach, 2005). The particular anion that forms is dependent upon the mole fraction of the reactants used. In most cases, a 1-alkyl-3-methylimidazolium chloride IL is mixed with aluminum chloride in varying ratios. Interestingly, chloroaluminate mixtures can be characterized as deep eutectic solvents that have markedly lower freezing and melting points relative to the starting IL. This is thought to be due to the stable complex formed between the halide anion
and inorganic salt, which delocalizes the charge on the anion (Freemantle, 2010). To date, the most common use of deep eutectic solvents has been for the electrodeposition of metals and alloys (Kirchner, 2009).

2.3 Synthesis and Properties of Chloroaluminates

2.3.1 Synthesis

As mentioned earlier, binary mixtures can be created that exhibit characteristics different from those of either constituent. The method first reported by Boon et al. for the preparation of chloroaluminate ionic liquids is still the preferred method used today (1986). In this synthesis method, a simple mixing of the Lewis acid (AlCl₃ and the halide salt (EMIMCl) is carried out under an inert atmosphere. The reaction is very exothermic and care should be taken when adding one reagent to the other; often, the inorganic metal halide is added step-wise in an attempt to reduce the evolution of gaseous products and heat. Excess local heat can result in the decomposition and discoloration of the new binary ionic liquid. The nature and chemical composition of the final product depends upon the proportion of the two reactions as shown in Figure 2-2(p. 16).

![Figure 2-2: Synthesis of Chloroaluminate](image)

\[
\text{EMIMCl} + \text{AlCl}_3 \rightarrow \text{EMIM-AlCl}_4 \quad (\text{EMIMCl in excess})
\]

\[
\text{EMIMCl} + \text{AlCl}_3 \rightarrow \text{EMIM-Al}_2\text{Cl}_7 \quad (\text{AlCl}_3 \text{ in excess})
\]

Figure 2-2: Synthesis of Chloroaluminate
2.3.2 Properties

The reaction of [EMIM]Cl, with AlCl₃, results in the formation of more than one anion species. When aluminum chloride is added in excess, the Lewis acidic anions [Al₂Cl₇]⁻ and [Al₃Cl₁₀]⁻ are formed (Dyson, Geldbach; 2005). Furthermore, the acidic eutectic mixture of EMIMCl and AlCl₃ in a ratio of 1:2 (mole ratio of n0.67) has a melting point of -96°C, compared to 87°C for pure EMIMCl alone. This phase behavior that is characteristic of chloroaluminate eutectic solvents can best be seen in Figure 2.3.2 (p. 18) (Fannin et al., 1984. Dyson, Geldbach, 2005). In instances where EMIMCl is the excess component, the resulting chloroaluminate is basic and both Cl⁻ and [AlCl₄]⁻ are present as anions. The melting point of this basic mixture, which results when the AlCl₃ ratio is less than 0.50, is only 7°C (Freemantle, 2010). However, in basic chloroaluminates, excess chloride deactivates the catalytic ability of the metal halide.

Despite the unique phase behavior demonstrated by EMIMCl-AlCl₃ mixtures, the other properties do not appear to be as nearly as surprising. For example, a 1:1 mole ratio exhibits a viscosity of 18 cP, which then decreases as the mixture becomes more acidic, as can be seen in Figure 2-4 (p. 19) (Wilkes et al., 1982) and Table 2.1 (p. 19). Typically, it can be said that the density of chloroaluminate ILs increases with increasing proportions of the aluminum halide. The polarity of imidazolium based ionic liquids such as the chloroaluminate studied in this thesis is very similar to that for methanol and ethanol. Thus, ILs are usually miscible with liquids that have medium to high dielectric constants. To be more specific, ILs based on 1-alkyl-3-methylimidazolium are miscible with water only when the number of carbon atoms in the linear alkyl chain ranges from 2-5. It is also important to note that unsaturated organic compounds are miscible with ILs, while saturated compounds are not (Kirchner, 2009. Freemantle, 2010).

Ionic liquids containing halide anions often provide enhanced catalytic activities
Figure 2-3: (a) Phase diagram of EMIMCl-AlCl$_3$; (Taken from Fannin et al., 1984). (b) Phase diagram of EMIMCl-AlCl$_3$; (Taken from Dyson, Geldbach, 2005).
Figure 2-4: Dependence of Absolute Viscosity upon EMIMCl Mole Fraction at 303 K; (Taken from Wilkes et al., 1982).

Table 2.1: Summary of Viscosity and Density of Varying Chloroaluminate Systems at 298°C (Obtained from Rogers, Brennecke, Seddon, 2007)

<table>
<thead>
<tr>
<th>Ionic Liquid System</th>
<th>Cation</th>
<th>Anions(s)</th>
<th>Temp, K</th>
<th>Viscosity (η), cP</th>
<th>Density, g cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>34.0-66.0 mole% [EMIM]Cl-AlCl₃</td>
<td>EMIM⁺</td>
<td>Al₂Cl₇⁻</td>
<td>298</td>
<td>14</td>
<td>1.389</td>
</tr>
<tr>
<td>50.0-50.0 mole% [EMIM]Cl-AlCl₃</td>
<td>EMIM⁺</td>
<td>AlCl₄⁻</td>
<td>298</td>
<td>18</td>
<td>1.294</td>
</tr>
<tr>
<td>60.0-40.0 mole% [EMIM]Cl-AlCl₃</td>
<td>EMIM⁺</td>
<td>Cl⁻, AlCl₄⁻</td>
<td>298</td>
<td>47</td>
<td>1.256</td>
</tr>
</tbody>
</table>
for carbon-carbon coupling reactions and many other organic substitutions and replacements. However, this is an exception to the rule, as halide anions have generally been found to inhibit catalytic activity. The catalytic activity of chloroaluminate ionic liquids depends on the acidity, and thus, upon the ratio between the [cation]Cl and the metal chloride. The ability of chloroaluminates to act as catalysts stems from the non-coordinating yet highly polar environment they afford to both reactants and catalysts. Traditional polar coordinating solvents form a complex on the active site of many homogeneous catalysts, therefore blocking the ability of the active site to perform catalysis. Thus, ILs with non-coordinating anions may be better suited for homogeneous catalysis, which would enable them to supplant the use of polar molecular solvents (Pretti et al., 2006. Kirchner, 2010).

2.4 Conclusion

It is clear that the properties and characteristics of chloroaluminate ionic liquids are extremely novel in many respects. Their essentially non-existent vapor pressures make them ideal candidates to replace molecular organic solvents and they can be customized for many particular processes as needed. It must be mentioned, however, that these ILs do exhibit a few drawbacks. All haloaluminate-based ionic liquids, particularly chloroaluminates, react vigorously with water or moisture. As a result, they decompose to form hydrogen halide gas (in our case hydrogen chloride gas) and corrosive hydrohalic acid (hydrochloric acid). This can then cause other problems related to the reaction products and the conditions in which the IL can be properly used. For instance, it may lead to the unwanted charring of biomass, which would then preclude the extraction of free fatty acids and any further reaction products.

Despite the disadvantages inherent in the use of imidazolium ionic liquids, they remain the most widely studied and well characterized of any ionic liquid class. It
may be argued that this is solely due to the fact that they are a member of the first generation of ionic liquids, but it remains that these ionic liquids have been able to perform numerous types of reactions with similar and even better results when compared to traditional solvents and catalysts.
Chapter 3

Analysis of Soy Flour Lipid Content and Composition

3.1 Introduction

In order to properly quantify the production of FAMEs resulting from transesterification reactions, the triglyceride content of the biomass needs to be determined. Traditional methods for quantification of the lipids and subsequent derived fatty acid methyl esters (FAMEs) present in biomass is typically an intensive and time consuming process. In this study we have developed a thermogravimetric analysis (TGA) based method to facilitate easy and accurate quantification of the lipid content of soy flour. It is hypothesized that this TGA method of lipid content analysis would be suitable for other oleaginous types of biomass, including algae.

3.2 Methods and Materials

The soy flour biomass was obtained from Shiloh Farms in New Holland, PA, which produces organically grown and processed soy products. The lipids in the soy flour biomass were extracted using sonication in a solvent mixture of equal parts hexane,
tetrahydrofuran, and chloroform by volume. The collected lipids were then analyzed on a Restek RTX-biodiesel column using a Shimadzu GC-2010 equipped with a flame ionization detector (FID). Monoolein, diolein, and triolein were used to generate standard curves for the lipids present in the biomass, allowing for the quantification of the lipid content present.

To conduct the fatty acid methyl ester analysis, approximately 100 mg of biomass was reacted with 5 mL of acidified (5 mol % sulfuric acid) methanol for 1 hour at 90°C. The resulting FAMEs were then extracted into hexane and reacted for an additional 15 minutes at 90°C to ensure that the reaction had run to completion (Nelson, 2009). Care was taken to see that the products had adequate time to be completely extracted while not being exposed to conditions that would result in product degradation. The samples were then analyzed for fatty acid methyl esters using an Agilent Durabond HP-99 column on a Shimadzu GC-2010 system equipped with a FID. FAMEs were quantified using a FAME-10 standard mixture (methyl palmitate, methyl linolenate, methyl linoleate, methyl oleate, methyl stearate) obtained from Sigma-Aldrich.

The TGA used was a TA Instruments TGA-Q50 with an alumina pan and nitrogen carrier gas. The instrument program utilized a simple ramp scheme of 20°C/min to a maximum temperature of 600°C, upon which reaching, would indicate the end of the run. The lipid content was determined through the weight loss that occurred between the temperatures of 360 and 420°C. A sharp derivative weight loss peak was observed between these temperatures, suggesting that the volatilization of lipids occurred over this range.

3.3 Results and Discussion

In order to properly analyze the content of the soy flour biomass, the appropriate lipid and FAME standards were calibrated, which then lead to the generation of stan-
standard curves; see Figures A-2 (p. 75) and A-3 (p.76) in Appendix A. Representative chromatograms of both lipid and FAME standards can also be found in Appendix A, Figure A-1 (p.74). The characteristic soy flour lipid and FAME chromatograms produced via the appropriate analyses can be found below in Figure 3.1 (p. 25). The specific content of each sample is described in further detail later in this section.

The data in Figure 3-2 shows the total lipid content in soy flour as determined through gas chromatography and TGA analysis. Gas chromatography was also used to determine the FAME content, which is the derived product of the triglycerides present in the biomass through transesterification using methanol. The oil content was found to average slightly above 20 percent of the total mass of the soy flour, which corresponds very well to the commonly accepted values found in the literature (Liu, 1997). Each analysis was performed in quadruplicate to ensure consistency within the biomass and data acquisition.

The average thermogravimetric data for the same biomass samples used in the other two analyses can be found in Figure 3-3. As can be seen, the weight loss that occurs between 360 and 420°C accounts for approximately 20.65% of the total mass of the soy flour samples; matching very well to both the lipid and FAME data. The first peak indicates the presence of proteins, the second peak is representative of carbohydrates, and the third peak is the lipid portion. While the soy flour content could have been properly analyzed through the lipid and FAME studies alone, the TGA data presents a third source of data that only serves to support the conclusions reached through gas chromatography.

The specific lipid and derived methyl ester content of the soy biomass was also determined to predict the types of fatty acid methyl esters that might be produced through Lewis acidic IL transesterification reactions. Through the lipid analysis conducted on the gas chromatograph, it was found that the soy flour lipid content was composed of 88% triglycerides, 7% diglycerides, and 5% monoglycerides;
Figure 3-1: (a) The lipid content of soy flour biomass consists primarily of triglycerides, with a nearly equal content of mono and diglycerides. A Restek RTX-Biodiesel Column (max. temp of 350°C) was used (b) Methyl oleate accounts for the majority of the FAMEs produced from the fatty acids present in soy flour. The FAME content was analyzed using an Agilent Durabond HP-88 column (max. temp of 250°C)
Figure 3-2: Soy flour lipid content for four samples as determined by lipid, FAME, and TGA analysis. The values correlate very well among the three methods and the accepted literature values.

Figure 3-4 (p. 27). The derived methyl ester content of the soy flour biomass was determined through a traditional transesterification method using acidified (sulfuric acid) methanol; please refer to Section 3.2. It was found that methyl oleate constitutes 54% of the total FAMEs produced from the biomass, while methyl linoleate, palmitate, stearate and linolenate account for 23, 12, 7, and 4% respectively; Figure 3-5 (p. 28). The fact that methyl oleate (C18:1) is the major methyl ester produced is of consequence, as it has the desired degree of unsaturation for the production of high-quality biodiesel (B-100) (Yang et al., 2010).

It had been desired that the biomass would consist primarily of triglycerides so as to provide favorable conditions for a shunt transesterification in contrast to the traditional three step process. A shunt reaction is beneficial because it mitigates and may even eliminate the stepwise production of diglycerides and monoglycerides from the breakdown of triglycerides and diglycerides, respectively. This would then benefit from a reduced level of glycerol formation as well as favorable reaction kinetics and
Figure 3-3: Peak (1) Protein (2) Carbohydrates (3) Lipid. The peaks are indicative of the degradation and loss of the respective content. The weight loss from 360 to 420°C is approximately 20.65 percent.

Figure 3-4: Lipid composition of soy biomass as determined through lipid analysis. Triglycerides account for 88 percent of the lipid content, while monoglycerides and diglycerides account for 5 and 7 percent respectively.
mass transfer properties.

Figure 3-5: Fatty acid methyl ester composition of soy flour biomass as determined through FAME analysis. The higher molecular weight methyl esters account for the majority of the esters produced as a result of the triglyceride rich lipid content.

3.4 Conclusions

The overall effectiveness of the thermogravimetric method for determining the triglyceride content of soy flour biomass has been demonstrated to be within 2% of the results obtained through the traditional methods of gas chromatography. Therefore, it is postulated that the protein and carbohydrate content of the soy flour may also be determined through TGA analysis.

Understanding the lipid content of the biomass used in the reactions described henceforth, allows for the proper analysis of the reactions and corresponding conditions. Therefore enabling us to make effective and knowledgeable decisions in an attempt to optimize the reaction for yield and energy efficiency. As a pinnacle of the
research conducted, it would be ideal to recover 20% of the mass by weight in the form of fatty acid methyl esters, indicating nearly 100% yield and conversion.
Chapter 4

Production of Fatty Acid Methyl Esters from Soy Flour using Lewis Acidic Ionic Liquids

4.1 Abstract

In this study, a method for in-situ production of fatty acid methyl esters directly from lipid-containing biomass (without prior extraction of oil) using a Lewis acidic ionic liquid was investigated. The IL served as both the solvent and catalyst in this system, which also included dichloromethane and methanol. The methanol was present in stoichiometric excess, much like traditional transesterification reactions, to drive the reaction to completion. Dichloromethane was used to dissolve and disperse the viscous IL, thus improving mass transfer rates as well as protecting the IL from water and preserving the Lewis acidity. The optimum reaction conditions were determined as ratios between solvents, IL requirements, and biomass solid concentration. Upon determination of the optimum reaction conditions, the reaction was tested for temperature and time dependency as well as for catalyst recovery and reuse. Lastly,
the fate of the remaining biomass constituents as a result of the reaction was determined.

4.2 Introduction

4.2.1 Traditional Transesterification

The production of fatty acid methyl esters, more commonly referred to as biodiesel, from vegetable oils has been explored vigorously for the past several years. The traditional processes involve the catalytic reaction of vegetable oils with short chain alcohols through alcoholysis or transesterification (Srivastava, Prasad, 2000). These two reactions are distinguishable due to the fact that in alcoholysis, a Lewis base acts as a nucleophile and performs the desired substitution to form an ester and glycerol. In contrast, a Lewis acid is typically employed in the more traditional transesterification reaction (Otera, 1993).

In transesterification, an ester is transformed into the mono-alkyl ester through reaction with an alcohol. This reaction proceeds in a stepwise manner, where the triglycerides are first converted to diglycerides, which then react to become monoglycerides. Finally, the monoglycerides are broken down to form the third ester and glycerol. The overall scheme can be seen in Figure 4-1(a)(p. 32) and the stepwise reactions are shown in Figure 4-1(b). The reaction is itself reversible, requiring that the alcohol be added in stoichiometric excess to ensure that the reaction kinetics favor conversion to the alkyl ester. The balanced stoichiometric formula requires three times as many moles of methanol to triglycerides, but it is common to use amounts that double and even triple that ratio (Schuchardt, Sercheli, Vargas, 1998; Wu et al., 2007).

While transesterification reactions have the ability to proceed on their own, they suffer from exceedingly slow reaction rates. Therefore, the addition of heat and
an acidic or basic catalyst is required. Currently, the use of a basic catalyst such as NaOH or KOH is often favored due to high yield, low corrosion, mild reaction conditions, and increased reaction rates (Freedman, Pryde, 1982). The one drawback of base catalyzed transesterification is that trace amounts of water in the alcohol and biomass may promote saponification, which not only produces undesirable soaps but also consumes the catalyst. Additionally, these alkaline homogeneous catalysts are difficult to recover and a large amount of wastewater is necessary to clean both the product and catalyst (Wu et al., 2007).

As a result of the issues related to the use of homogeneous catalysts, researchers have made efforts to create effective heterogeneous catalysts. The development of these catalysts has led to the study of biological enzymes, ion-exchange resins, alkylguanidines and ionic liquids, among others. However, many of these methods suffer from low activity, high temperatures, long reaction time, high cost, or high toxicity.
Therefore, it would be ideal to develop an acid catalyzed transesterification reaction that allows for the reuse of the catalyst while producing biodiesel in a system that preferentially partitions the glycerol into a phase separate from the desired products (Neto, et al., 2007).

### 4.2.2 In Situ Transesterification using Ionic Liquids

In general, there are two methods through which the extraction and catalytic conversion of the triglycerides present in biomass feedstocks can be approached, (1) extraction followed by transesterification and (2) in situ transesterification, see Figure 4.2.2 (p. 33).

Figure 4-2:  (a) Lipid extraction is energy intensive, particularly when considering algae feedstocks (b) In situ transesterification utilizes reactive extraction and makes product recovery simpler

The first method requires that the triglycerides first be extracted from the biomass and then converted to fatty acid esters using a catalyst and alcohol. However, ex-
tracting the lipid content from biomass can be energy, particularly from oleaginous microbial feedstocks such as algae. Consequently, it would be beneficial to develop in situ transesterification methods. The ability of ILs to act as both solvent and catalyst makes them a good choice for in situ transesterification of biomass lipids. Lewis acidic ILs are especially well suited for reactive extractions of this type, as their properties enable them to effectively solvate as well as catalyze the esterification of biomass lipids.

As a first step towards developing this approach, we used chloroaluminate ILs to perform in situ transesterification reactions. EMIMCl-AlCl$_3$ systems are well studied for other applications, relatively inexpensive and easy to synthesize, and thus provided a simple catalytic system with which to begin.

It should also be noted that others have explored the use of chloroaluminate ILs in various reactions. Earle and Seddon describe the chemical behavior of Franklin acidic chloroaluminate ILs (where X(AlCl$_3$)>0.50) as that of a powerful Lewis acid (2000). The advantage of these ILs is that they promote the same reactions that are traditionally carried out with aluminum chloride, but do not suffer from the disadvantage of the low solubility of aluminum chloride in many solvents (Earle, Seddon, 2000). The work of Liang et al. (2008) has also demonstrated that the most effective Lewis acid for the transesterification of soy oil was in fact AlCl$_3$, which resulted in much higher yield compared to iron, zinc, tin, and magnesium halides. This very work also concluded that EMIMCl provided the best catalytically active cation, as it was found that the activity decreased as the length of the hydrocarbon chain increased.

In a separate study, the use of Bronsted acidic ILs to transesterify cottonseed oil was explored by Wu et al., (2007). It was found that these catalysts were nearly as active as concentrated sulfuric acid but could be recovered and recycled. However, these ILs required temperatures of 180°C for four hours to achieve over 90% yield.
Similar reaction conditions were needed when using Bronsted acidic ILs to prepare biodiesel from waste oils (Han et al., 2009). When compared to the more mild reaction conditions used by Liang et al., (70°C for 9 hours) it is reasonable to hypothesize that ionic liquids with inherent Lewis acidity may provide a more active and stable system for the transesterification of triglycerides (Neto et al., 2007).

4.3 Materials and Methods

4.3.1 Materials

The ionic liquid, EMIMCl, purity >98%, was obtained from Tokyo Chemical Industry USA. This specific synthesis of EMIMCl was white and crystalline in form and had a water content regularly found to be <3300 ppm as determined by Karl Fischer titration. The aluminum chloride was purchased from Sigma Aldrich with a purity >98%. The extracting solvent, hexane, and the co-solvent, dichloromethane, were from EMD chemicals with a purity of at least 98%. The gas chromatography systems utilized were both Shimadzu GC-2010 models equipped with a flame ionization detector and a Restek RTX-biodiesel and Agilent Durabond HP-99 column, respectively. The GC-MS analysis was carried out on a HP 5973 GC-MS equipped with a Restek 5-Amine column.

4.3.2 Methods

4.3.2.1 Chloroaluminate Synthesis

Due to the high moisture sensitivity of the chloroaluminate solvent/catalyst, the ILs were carefully and extensively dehydrates; the experimental set-up was also designed to prevent water from entering the reaction mixture. For dehydration, the EMIMCl was dried in a rotary evaporator for 3 hours at 85°C under a vacuum of
150 MPa. The molten EMIMCl was then transferred to a 20 mL serum bottle and kept under a constant stream of nitrogen flowing at 4 psi. The appropriate amount of aluminum chloride was then added to the EMIMCl to make the eutectic mixture of chloroaluminate commonly referred to as n0.67. The acidity of the chloroaluminate depends upon the anion and its concentration within the synthesized IL. When the AlCl$_3$ mole fraction is <0.50, the chloroaluminate is not acidic and is likely to result in poor catalytic conversion of the triglycerides. In this study, we used n0.67 for most experiments, based upon the fact that others had optimized their reaction using n0.70, (Liang et al., 2008). In our case, the lower melting point of n0.67 compared to that of n0.70 made it more suitable for temperature range utilized in this work. It was believed that n0.67 would be sufficiently active and higher mole fractions of AlCl$_3$ would only be needed if the experimental data demonstrated a compelling trend for the use of more acidic catalysts.

Adding aluminum chloride to the EMIMCl results in an exothermic reaction. To prevent overheating, the addition of aluminum chloride was carried out in a uniform stepwise fashion and the mixture was kept in an ice bath with stirring for the first 15 minutes. The mixture was then allowed to warm to room temperature and then heated to 60°C, increasing the solubility of the AlCl$_3$ in EMIMCl. After 60 minutes, the chloroaluminate mixture was removed from the heat source and sealed under nitrogen in a gas tight vial until needed. The density of the synthesized chloroaluminate IL was found to average 1.30 g/mL at 296K, which is slightly lower than other reported values (see Table 2.1(p. 19).

4.3.2.2 Transesterification Reaction and Product Analysis

The reactions were carried out in a 10 mL glass vial and stirred with a triangular stir bar designed for mixing viscous reactions. After the appropriate amount of soy flour had been added, the selected ratio of IL/methanol/dichloromethane was added.
The contents of the vial were then purged under nitrogen for 3 minutes and placed in a silicon oil bath at the required temperature, which was held constant by a thermocouple and calibrated with an external thermometer. Each reaction was stirred for the entire duration at 125 rpm, removed from the oil bath, and then allowed to cool to room temperature. It is important to allow the reaction to cool due to the high volatility of the dichloromethane co-solvent. The samples were then centrifuged and the supernatant collected, from which the products were then extracted using hexane and prepared for gas chromatography and mass spectroscopy analysis.

The NMR analysis was conducted using an INOVA-600 equipped with a HC/N with XYZ-PFG probe. The deuterated solvent of choice was chloroform, as it solubilized the EMIMCl and allows for a high lock-level compared to acetone for this particular instrument.

The remaining (unspent) soy flour solids were washed with water and allowed to dry in an oven at 40°C. The unextracted lipid content was quantified using triglyceride, FAME, and TGA analysis to complete the lipid based carbon balance.

4.4 Reaction Optimization

4.4.1 The Impact of the Co-solvent

Reactions carried out in IL media can be hampered by the high viscosity of this reaction media, which can then result in inefficient mixing. The IL utilized in the reactions reported here (EMIMCl-AlCl₃) has a viscosity of approximately 14 cP, Figure 2-4(p. 19). The viscosity and mixing characteristics are even more adversely affected when solids are added to the reaction media due to the formation of viscous slurries. Our preliminary tests in this viscous medium showed poor conversions and yields.

We hypothesized that reaction kinetics and yields could be improved if the viscos-
ity was decreased. To verify this hypothesis, we diluted our reaction media through the addition of co-solvents, which was later found to be somewhat similar to what could be inferred from a publication by Cooney and Young (2009). Because all organic solvents are not soluble in ILs, the ability of various solvents to solubilize the acidic chloroaluminate and form a homogenous system upon the addition of methanol was explored first. Of the solvents tested in these preliminary tests, our results showed that dichloromethane, ethyl acetate and chloroform formed a homogeneous mixture with chloroaluminate and methanol. Interestingly, chloroform is only slightly soluble with chloroaluminate, but upon addition of methanol, the mixture forms a homogenous solution.

Figure 4-3: The impact of different organic co-solvents under similar reaction conditions. All reactions were run in 1 mL methanol, 0.1 mL IL, and 1 mL solvent at 90°C with 10 percent solids.

Transesterification reactions were performed by heating mixtures of chloroalumini-
nate, methanol, solvent and biomass to 90°C. As can be seen in Figure 4-3, the difference in conversion and yield between ethyl acetate and the other two solvents is significant, particularly after 2 hours of reaction. Although product yields in chloroform- or DCM- containing reactions appear similar, DCM solubilized more triglycerides than chloroform. DCM also has a lower boiling point than chloroform and may be easier to separate and recover from spent reaction media. Finally, DCM is also considered to be the least toxic of the chlorohydrocarbons (Rioux, Myers; 1988).

Figure 4-4: The impact of varying the volume of co-solvent. All reactions were run in 1.0 mL methanol and 0.1 mL IL at 90°C with approximately 330 mg of biomass for 4 hours.

The addition of dichloromethane (experimental optimum of 0.50 mL) to the reaction mixture serves to disperse the IL and mitigate mass transfer limitations. Without the presence of this co-solvent, the acidic IL is unable to effectively disperse throughout the reaction media, resulting in poor conversion. To the best of our knowledge, such an approach to lowering the viscosity through addition of co-solvents while maintaining their catalytic activity has not be previously reported in the literature. Again,
the work of Cooney and Young (2009) may be similar, but few details are actually elucidated in the report so as to hamper any conclusive comparison.

4.4.2 Time and Temperature

After arriving at an optimum reaction media constitution, we tested the effects of time and temperature to estimate the optimal reaction conditions. Although reaction rates increase with a corresponding increase in temperature, elevated temperatures can result in undesirable product degradation or side reactions. Thus, determining the effect of temperature and time is not only important to optimize product yield, but also to increase energy efficiency and minimize the potential for product degradation.

![Graph showing the impact of reaction time and temperature on the yield of fatty acid methyl esters.](image)

Figure 4-5: The impact of reaction time and temperature on the yield of fatty acid methyl esters. All reactions were run in 1 mL methanol, 1.0 mL DCM and 0.1 mL IL with approximately 330 mg of biomass

In general, there is a significant difference in product yield between reactions that are run for two and four hours respectively, a trend that can be seen in Figure 4-5(p. 40). The observed improvement in yield is nearly 20%, thus, it can be argued that it is more cost effective to run the reaction for four hours as compared to two.
This data agrees well with the literature reports of similar reactions, where yield even decreases after six hours (Liang et al., 2008; Neto et al., 2007). While the impact of time and temperature on the production of methyl esters was first studied using what would become an unoptimized ratio, the typical trend discovered in this preliminary research was found to apply to the optimized ratio as well. This can be seen in section 4-7, where the 4 hour reactions easily outperform those run for 2 and 6 hours respectively.

Additionally, a range of temperatures from 90 to 120°C were studied to determine if the reaction would proceed at lower temperatures. It was found that product conversion was dependent upon temperature in the order of 110°C >120°C >100°C >90°C. Based on this data, 110°C appears to be the optimum temperature for the conversion of biomass triglycerides into FAMEs. It is likely that this temperature does not cause significant product degradation, which is thought to be responsible for the decreased yield observed at 120°C.

4.4.3 Chloroaluminate and Methanol Catalysis

Once it had been found that the use of an organic co-solvent was advantageous, the particular catalyst/alcohol ratios were optimized based on product yield. To do this, the effect of the volume of IL catalyst was investigated without altering the volume of the co-solvent. As can be seen in Figure 4-6(a)(p. 42), the amount of product recovery, particularly as methyl esters, is dependent upon the volume of acidic chloroaluminate catalyst added. Without the presence of the catalyst, the liberated triglycerides do not undergo transesterification and no methyl esters are produced.

The volume of acidic catalyst used had a linear impact on the production of methyl esters and extraction of lipids in the range of 0.02 to 0.10 mL. However, increasing the IL volume to 0.25 mL did not result in significant improvement in either the production of FAMEs or extraction of lipids - possibly due to the high viscosity of
Figure 4-6: (a) All reactions were run in 1.0 mL methanol and 1.0 mL DCM at 90°C with approximately 330 mg biomass for 4 hours (b) All reactions were run with 0.1 mL IL and 1.0 mL DCM at 90°C with approximately 330 mg biomass for 4 hours
the reaction media in the presence of such high amounts of IL. In fact, it can be seen that adding as much as 0.5 mL of catalyst is no more effective than adding 0.04 mL when all other conditions are held constant. Therefore, when considering the cost of ILs, the optimum volume of catalyst was found to be 0.10 mL. A similar progression was seen by Liang et al., and Wu et al., but was explained using the concept of catalytic active sites. In effect, they hypothesized that there were not enough active sites for the reaction to take place when the catalyst amount was too low, but that the reverse reaction occurred when there was an excess of catalyst present (2008; 2007).

The addition of an alcohol is necessary for any transesterification reaction to proceed. Typically, the stoichiometric production of biodiesel requires three times as many moles of methanol compared to triglycerides, Figure 4-1(a)(p. 32). However, in similar IL catalyzed reactions found in the literature, a molar ratio of methanol to oil of 30-150:1 was needed (Liang et al., 2008). Based upon the determined triglyceride content of the soy flour biomass and the distribution of the derived methyl esters, it was hypothesized that the reaction of interest would proceed using a stoichiometric ratio of 3:1 (by mol) of methanol to oil.

In order to test for the optimum volume of methanol needed, all other variables were held constant. As can be seen in Figure 4-6(b)(p. 42), increasing the volume of methanol does not have the same linear effect as was experienced when testing the catalyst volume. As expected, without the presence of the alcohol, the desired transesterification reaction does not occur. Interestingly, the methanol volumes of 0.25, 0.50, 0.75, 1.0 and 1.25 mL correspond to a stoichiometric excess of methanol of 28, 56, 84, 112 and 140 (by mol) respectively. While this excess is far greater than that expected by the hypothesized ratio, it agrees with the ratios used by others (Ranganathan, Narasimhan, Muthukumar, 2008). The collected data demonstrates maximum conversion at 112x (by mol) excess methanol, with a slight decrease at higher excess ratios. Thus, 1.0 mL of methanol was selected as the optimum for the
reaction of interest.

4.5 Effect of Biomass Concentration and Time

The data presented in the preceding sections clearly indicates that the optimum liquid ratio for the conversion of triglycerides to methyl esters in this system is 0.1/0.5/1.0 mL (IL:DCM:MeOH). Despite the preliminary tests regarding the impact of time, it was decided that it would be advantageous to test the effect of both time and biomass concentration at the newly determined ratio.

![Graph](image)

**Figure 4-7:** All reactions were run with 0.1 mL IL, 0.50 mL DCM and 1.0 mL MeOH at 110°C

To do this, the reactions were run at the optimum temperature of 110 °C using the before mentioned ratio while varying the biomass solid concentration (%w/w) and reaction time. This would then demonstrate the true ability of the determined solvent ratio to perform the desired reaction and aid in finding the most effective biomass
concentration and reaction time. The data presented in Figure 4-7 (p. 44) shows that nearly complete conversion (>90%) is achieved in the 4h reactions consisting of 5, 10, 15, and 20% biomass solids. In fact, running the reaction for four hours results in an increase in FAME conversion of nearly 20% compared to the 2h reaction, while increasing the time to 6h is typically detrimental, which was also seen by Neto et al. (2007). This data agrees with that previously described in section 4.4.2, and therefore demonstrates that four hours may be near the optimal reaction time.

The conversion of triglycerides to methyl esters does not appear to be significantly affected by increasing the biomass concentration from 5 to 20% (w/w). Product yields, however, begin to decrease at 25% (w/w) solids. Similarly, in the DCM tests, the optimum solvent ratio indicated an effective solids concentration of 20% (w/w); Figure 4-4 (p. 39). Since higher solids concentrations result in lower downstream processing costs, the data suggests that 20% (w/w) is the highest biomass concentration that can be processed through the reactor without affecting product yields.

4.6 Reactions in Series

The ability of the chloroaluminate catalyst to perform additional transesterification reactions was explored in order to ascertain reusability of the IL. This was accomplished by running reactions in series and determining the overall product yield for all of the sequential reactions. To do this, each reaction was run using the conditions described at the end of section 4-7. After each reaction, the contents of the vial were centrifuged and separated into the liquid and solid fractions. The volume of the recovered liquid fraction was determined and the lost volume was replaced by a mixture of chloroaluminate and DCM in the optimized 5:1 ratio. It must be noted that methanol was not replaced in each series because it was present in great stoichiometric excess. In nearly all cases, as much as 85% of the original liquid volume
(1.6 mL) was recovered.

Figure 4-8: All reactions run at 110°C for 4 hours. No products were extracted in previous series reactions. Lost liquid volume was replaced using DCM and IL in a 5:1 ratio.

The products were only extracted after the reaction had proceeded through its respective number of series, meaning that the FAME product accumulated within the system. This was not considered to be problematic, as others had run similar reactions using pure vegetable oils, which consists solely of fatty acids, and did not report saturation of the system (Liang et al., 2008). Calculation of the recovered FAME was cumulative (w/w) across the respective number of series.

Figure 4-8(p. 46) demonstrates that the overall product yield decreases with each subsequent reaction in series. Again, the biomass concentrations ranging from 5 to 20% (w/w) performed almost identically while reactions containing a higher biomass content experienced a significant loss of conversion. In general, running the reactions four times in series caused a notable decrease in product conversion, resulting in as much as a 50% loss. Interestingly, the greatest product loss occurred as a result of
the second series, which indicates that it is not efficient to run the transesterification reaction more than once without recovering the product and catalyst.

In order to further optimize the reaction conditions, additional series reactions were carried out using: (1) a more acidic chloroaluminate catalyst; and others in which the lost volume was replaced by: (2) dichloromethane, (3) the appropriate MeOH:DCM:IL ratio. These results, presented in Figure 4-9(p. 47), reveal that using a more acidic chloroaluminate catalyst (n0.72) does not impart improved catalytic activity or increased levels of product conversion. In fact, a more acidic ionic liquid may predispose the biomass to charring and be more susceptible to water contamination.

Figure 4-9: All reactions run at 110°C for 4 hours. No products were extracted in previous series reactions. It is necessary to replenish the consumed chloroaluminate with each series in the appropriate DCM:IL ratio. Adding MeOH to the recovered liquid volume does not improve product conversion. Using a more acidic ionic liquid does not appear to be beneficial.

The data also suggests that it is necessary to replenish the lost liquid volume using the IL catalyst in the befitting DCM:IL ratio. Simply using DCM alone to recharge
the liquid volume culminates in a nearly complete loss of conversion after four series. Therefore, it can be concluded that sufficient amounts of IL were not transferred to subsequent steps or that catalytic activity was diminished as a result of dilution. It is also possible that the IL experienced a level of degradation during the reaction, resulting in diminished amounts of active catalyst being present in further steps of the series. Lastly, replacing the lost volume with the appropriate MeOH:DCM:IL ratio does not improve product conversion, which is due to the fact that the methanol is present in excess.

4.7 Reaction Products

The desired reaction products of any transesterification reaction are esterified fatty acids that can be used as fuel in diesel equipment without further processing or modifications to the engine. Figure 4-10(a)(p. 50), shows a representative GC chromatogram of the reaction products quantified in this study. The methyl esters are identified in the figure itself, and the elution times of each product can be compared directly to those of the standards as seen in Figure A-1(b)(p. 74). Interestingly, the identity of two unexpected peaks, identified as a sulfur and nitrogen compound respectively, were verified using a HP GC-Mass Spectrometer with a Restek-5 Amine column; Figure 4-10(b)(p. 50).

The sulfur compound, which was determined to be 1-(2-Thienyl)-1-propanone (C\textsubscript{7}H\textsubscript{8}OS) had a confidence value of only 49%, Figure A-4(a)(p. 77). However, it is likely that this is indeed a sulfur compound, as the thiamine vitamin and corresponding phosphate derivatives present in unprocessed soy flour may be responsible for this peak.

Likewise, the GC-MS was only able to provide a confidence level of 38% for the nitrogen compound, which was identified as 4-amino-5-ethyloxycarbonyl (C\textsubscript{6}H\textsubscript{9}N\textsubscript{3}O\textsubscript{2}),
Figure A-4(b)(p. 77). The structure of this compound contains a ring very similar to that of the EMIMCl present in the chloroaluminate, but contains a third nitrogen. This compound may result from the degradation of the EMIMCl as a result of the reaction. However, this compound may also be an amino-acid derivative resulting from the extraction and breakdown of proteins present in soy flour. Interestingly, the relative size of the nitrogen peak was found to be somewhat temperature dependent, and was studied further to determine if 110°C was in fact the optimum reaction temperature.

As can be seen in Figure 4-11 (p. 51), at 110°C, the amount of the nitrogen compound present in the extracted products is greatest, correlating to the highest conversion of fatty acids to methyl esters. A possible explanation is that this operating temperature may be the prime temperature for the extraction of the proteins present in the soy flour biomass. However, the assumption would then follow that higher temperatures (120°C and above) result in protein denaturation and therefore the decreased amount seen at those temperatures. Nonetheless, because the amount of nitrogen product present in the reaction carried out at 110°C is not appreciably greater than that at other temperatures, it was determined that the marked increase in biodiesel production at this temperature far outweighs any negative consequences that it may otherwise cause.

The Lewis acid catalyzed transesterification reaction results in a product composition nearly identical to that obtained using acidified methanol; refer to Figure 4.12 (p. 52). Thus, the reaction mechanism is the same for both systems and there is no preferential product formation despite the differences in catalyst and the use of a co-solvent. The product composition indicates that it consists of 52% methyl oleate (C18:1), which is the desired FAME in pure biodiesel (Knothe, 2005; Yang et al., 2010). Increased amounts of methyl oleate leads to improvement in the oxidative stability of biodiesel. Additionally, the decreased degree of unsaturation will result in
Figure 4-10: (a) Typical reaction products obtained from the Lewis acid catalyzed transesterification of soy flour. An Agilent Durabond HP-88 column (max. temp of 250°C) was used (b) The fatty acid methyl ester and phenyl compounds were identified with over 90% confidence using a Restek-5 Amine GC-MS column
Figure 4-11: The nitrogen peak at different temperatures and reaction times. The optimum solvent ratio and biomass concentration were used.

a higher octane number, decreased NO\textsubscript{X} emissions as well as favorable cold properties (McCormich et al., 2001; Knothe, 2005).

It is thought that the chloroaluminate system enables the triglycerides within the biomass to undergo a shunt reaction. This is supported by the fact that there are no unreacted monoglycerides or diglycerides present in the extracted reaction products. Interestingly, others have accounted for the occurrence of shunt reactions when using methanol as the alcohol of choice. Freedman, Butterfield, and Pryde found that using methanol to catalyze the transesterification of soybean oil resulted in a shunt reaction that had two regions, one that was ruled by mass transfer while the other was kinetically controlled (1986).
(a) Composition of fatty acid methyl esters recovered through traditional transesterification

(b) Composition of fatty acid methyl esters produced via the chloroaluminate catalyzed transesterification

Figure 4-12: (a) Composition of the methyl esters obtained through traditional transesterification of soy flour. (b) Composition of the fatty acid methyl esters recovered through transesterifications carried out in ionic liquid media
4.8 Spent Biomass Characterization and the Triglyceride Carbon Balance

Much like in section 3.1, it is necessary to characterize the content of the spent biomass. Through analyzing the content remaining within the biomass, it is possible to complete a carbon balance of the triglycerides in the system as well as determine possible uses for the spent biomass. Additionally, determining the triglyceride content of the spent biomass may serve to validate the reaction product data by demonstrating that the total triglyceride balance does not exceed 21%.

The triglyceride, FAME, and TGA analysis methods first described in section 3.2 were used to quantify the content of the spent biomass. The biomass solids were separated from the reaction media supernatant after centrifugation and washed with water until the washings did not show any visual indication of leached products from the solid residue. The solids were then allowed to dry in an oven under low heat at 40°C for 48 hours. Due to issues with solids recovery in samples containing less than 200 mg of soy flour, the spent biomass from these samples was not analyzed. Nonetheless, duplicate data was obtained using each of the three methods of analysis for the reactions containing 15, 20, 25 and 30% solids (m/m).

The recovered spent biomass, which can be seen in Figure 4-13(p. 54), contains a layer of proteins and chloroaluminate that sits on top of the spent soy flour. In all cases, the recovered biomass was collected and analyzed through thermogravimetric analysis first before conducting the respective chromatography tests. This was done in order to gauge the type of results that should be expected through the triglyceride and FAME analyses.

The TGA data; Figure 4-14(a)(p. 55), compares the derived weight profiles of soy flour to that of the spent soy flour. It is clear that peaks 1 and 3 are missing from the spent soy flour, indicating that the protein and lipids were extracted as
result of the reaction. In fact, from 360 - 420°C, the spent biomass incurred only a 3.5% loss in weight, compared to that of 20% for the unreacted biomass. However, peak 2, carbohydrate, is still present within the spent biomass and may present an opportunity for additional uses in the growth of simple cells, animal feed, or for use as a glue for the bonding of paper (NNFCC, October 2011).

The data obtained from the lipid and FAME analyses were compared against each other as well as the TGA data. This can be seen in Figure 4-14(b) (p. 55), which indicates that all three analyses provide consistent and accurate results. As expected, the lipid content remaining within the spent biomass increases at a solids concentration of 25% (w/w), correlating to the substantial decrease in FAME yield experienced at that concentration. Additionally, this analysis allows for the completion of the triglyceride carbon balance, which will reflect the accuracy of this entire paper, as the content can not exceed the approximately 20% present in unreacted soy flour biomass.

The triglyceride carbon balance was completed by taking the average values for the recovered FAME, recovered triglycerides, and unextracted triglycerides for the
Figure 4-14: (a) Peaks 1 and 3 indicate the nearly complete extraction of the protein and lipid, respectively, present in soy flour as a result of the transesterification reaction. Peak 2 shows that the carbohydrate content is only slightly diminished (b) Triglyceride, FAME, and TGA analysis of the lipid content remaining within the spent soy flour.
Figure 4-15: The triglyceride carbon balance is closed at approximately 20% of the total biomass. This value agrees with the triglyceride content found in unreacted soy flour biomass 4h reactions run at 110°C in the optimum liquid ratio. Figure 4-15(p. 56), shows that the triglyceride carbon balance has been closed at approximately 20% for all of the reactions tested, as expected. Once again, both the recovered and unextracted triglycerides increase significantly when the solids concentration reaches 25% (w/w), supporting the finding that the optimum biomass concentration is 20% (w/w).

4.9 Ionic Liquid Recovery

The economic viability of any process depends heavily upon the value of the products, reactants, catalysts, and the general costs of production. The re-use of unspent reactants and catalysts would not only decrease the production cost, but would also improve the environmental sustainability of the overall process.

Traditional transesterification reactions using organic acids are based upon homogeneous catalysis, which typically suffer from problematic recovery of the products
and catalyst. Therefore, it is desirable to develop heterogeneous processes that will allow the system to benefit from the advantageous of both catalytic schemes. In fact, one of the benefits of using ionic liquid catalysts in transesterification reactions is that they create a bi-phasic system from which the methyl ester products can be easily separated from the biomass, vegetable oil, glycerol by-product and catalyst (Liang et al., 2008).

Since ILs are fairly expensive, we investigated the potential for recovery of the IL catalyst from our reaction systems. Propitiously, it was found that the EMIMCl utilized in the synthesis of the Lewis acidic chloroaluminate precipitates out of the solvent (MeOH, DCM, chloroaluminate) mixture after the addition of hexane, which serves as the final extracting solvent. Figure 4.9(p. 57), shows the formation of a white precipitate in all three samples four hours after the addition of hexane. Nearly 75% of the original mass of EMIMCl used in the chloroaluminate was recovered as the precipitate, which was subsequently analyzed using $^{13}$C Nuclear Magnetic Resonance (NMR). It is presumed that the AlCl$_3$ remains solubilized within the solvent mixture.
and can not be recovered. However, this is of little concern, as aluminum chloride is relatively inexpensive and widely available.

The predicted and experimental NMR spectra for an EMIMCl standard as well as the precipitated EMIMCl can be found in Appendix A (p. 78). The results of the NMR study can be found below in Table 4.1. As can be seen, the predicted peaks correspond very well to those of the EMIMCl standard, which then closely match those of the precipitated EMIMCl. However, the recovered EMIMCl does appear to contain an unidentified impurity at 11.64 ppm. Nonetheless, based upon the NMR data alone, it can be concluded that the precipitate is indeed EMIMCl. As a way to further verify the proposed identity of the precipitate, the density and melting point of the precipitate were determined to be 1.135 g/mL at 80°C and 78-81°C respectively. This is in close agreement to the values of 1.112 g/mL at 80°C and 77-79°C provided on the EMIMCl MSDS sheet (1-Ethyl-3-methylimidazolium Chloride, MSDS, 2008).

Table 4.1: Summary of the $^{13}$C NMR Data for EMIMCl

<table>
<thead>
<tr>
<th>Predicted EMIMCl Peaks (ppm)</th>
<th>Standard EMIMCl Peaks (ppm)</th>
<th>Identity</th>
<th>Precipitated EMIMCl Peaks (ppm)</th>
<th>Identity</th>
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</thead>
<tbody>
<tr>
<td>136.62</td>
<td>137.54</td>
<td>EMIMCl</td>
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<td>124.11</td>
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<td>122.08</td>
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<td>36.76</td>
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</tr>
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<td>77.41</td>
<td>Chloroform-d</td>
<td>15.87</td>
<td>EMIMCl</td>
</tr>
<tr>
<td>77.20</td>
<td></td>
<td>Chloroform-d</td>
<td>14.33</td>
<td>Hexane</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11.64</td>
<td>Unidentified</td>
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<tr>
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<td></td>
<td></td>
<td>77.08</td>
<td>Chloroform-d</td>
</tr>
</tbody>
</table>
4.10 Conclusions

As a result of the experimental evidence described in detail in the preceding pages, it has been concluded that Lewis acidic chloroaluminates act as both an effective and efficient solvent and catalyst in the transesterification of soy flour. To the best of our knowledge, similar reactions have only been carried out using vegetable oils, not biomass solids. Additionally, the method proposed here utilizes a co-solvent that acts to solubilize the IL and reduce mass transfer limitations. It is clear that the use of an organic co-solvent makes this a novel reaction that benefits from catalyst recovery and reuse.

The optimized reaction achieved nearly 100% conversion to fatty acid methyl esters after four hours at 110°C. While this process requires a high reaction temperature, the reaction is fairly rapid and produces high yield, especially when considering that the substrate is solid biomass. In comparison, other systems require 9 hour reactions at 70°C for a comparable yield using soybean oil (Liang et al., 2008). It was found that the solvent/catalyst mixture of interest is capable of converting soybean oil to methyl esters, and it is believed that it may provide noteworthy benefits compared to other systems being studied.

Both Liang et al., and Wu et al., were able to demonstrate that the IL catalyst used in their respective systems performed well compared to many traditional homogeneous catalysts, making ILs an ideal choice due to their yield, product purity, and simple recovery and reuse (2008, 2007). Similarly, reactions using traditional acidified methanol methods achieve nearly complete conversion at 117°C in 3 hours or 20 hours at 77°C (Freedman, Butterfield, Pryde, 1986). Thus, the real benefit of ionic liquids resides in product separation and catalyst recovery rather than conversion.

A processing scheme for the transesterification reaction is proposed in Figure 4-17(p. 60). Because the starch content of the biomass is not extracted during the reaction, it may be utilized in other processes that can add value to the production
of biodiesel. Furthermore, the presence of any proteins may be washed from the spent biomass and recovered for use in the production of pharmaceuticals, dietary supplements, and animal feed.

Figure 4-17: Proposed Processing Scheme for Methyl Esters and Remaining Biomass

On the whole, the production of methyl esters from soy flour, acting as a surrogate for algae, has been demonstrated on a laboratory scale in a relatively simple process with high yield and mild reaction conditions. A potential pathway for catalyst recovery has also been shown. However, scale-up of both the reaction and catalyst recovery steps still needs to be carried out before commercial application of this method becomes feasible.
Chapter 5

Production of Acrylates from Biomass using Lewis Acidic Ionic Liquids

5.1 Abstract

The catalytic conversion of soy flour triglycerides to fatty acid methyl esters has been accomplished, but the manufacture of value-added products remains a vital component to the large scale production of biodiesel. It is now proposed that the chloroaluminate ionic liquids are able to perform acylation and metathesis reactions at low temperatures, and as such, may become an efficient alternative to the energy intensive practices of hydrocarbon cracking and dehydrogenation for the production of industrially relevant alkenes (Roberts et al., 2001).

The reaction of interest was run at 90°C for 2 hours in an inert atmosphere and it was found that the reaction products consisted exclusively of dodecyl acrylate, (Figure 5-1 (p. 62)), the presence of which was confirmed using gas chromatography-mass spectroscopy (GC-MS) and nuclear magnetic resonance (NMR) spectroscopy. How-
ever, the reaction was extremely difficult to replicate and the product could not be accurately identified based upon elution time using gas chromatography. It was eventually discovered that the dodecyl acrylate was actually present in the unprocessed soy flour biomass itself, but may still provide a unique opportunity for producing polymer precursors from biomass.

![Structure of Dodecyl Acrylate](obtained_from_NIST_Chemistry_WebBook)

**Figure 5-1: Structure of Dodecyl Acrylate (Obtained from NIST Chemistry WebBook)**

### 5.2 Introduction

The project discussed herein utilized a deep eutectic solvent, which was created by mixing 1-ethyl-3-methylimidazolium chloride (EMIMCl) with aluminum chloride in strategic ratios under an inert atmosphere. This process was first outlined by Welton in a 1999 literature review. The solvent, which also acted as a Lewis acidic catalyst, was used to catalyze the production of polymer precursor acrylates from soy flakes under mild reaction conditions. To the best of our knowledge, the production of dodecyl acrylate using ionic liquids has not yet been discussed in the literature, however, many researchers have alluded to similar research aspects in other papers focused on the utilization of chloroaluminate liquids (Boelhouwer, Mol, 1984; Roberts et al., 2001; Welton, 2004). The issue with using chloroaluminate ionic liquids is that these liquids are highly susceptible to water contamination and the subsequent production of hydrochloric acid and aluminum oxides. As a result, many have come to believe that the practical utility of EMIMCl is severely limited. Fortunately, carrying out the reaction in an inert atmosphere mitigated this problem and may be a simple
solution that will allow for the increased use of chloroaluminates.

5.3 Materials and Methods

5.3.1 Materials

The ionic liquid EMIM\textsubscript{Cl} was obtained from Tokyo Chemical Incorporation USA. This specific synthesis of EMIM\textsubscript{Cl} had a water content regularly found to be $<3300$ ppm by Karl Fischer titration and was in a white crystalline form. The aluminum chloride was purchased from Sigma Aldrich with a purity of $>98\%$. The extracting solvent, chloroform, was from Acros Organics and the product standard was obtained from Polysciences, Inc. The AlCl\textsubscript{3} was added in excess to dry solid EMIM\textsubscript{Cl} and the resulting chloroaluminate was prepared following the procedure outlined in the literature (Welton, 1999). The gas chromatograph utilized was a Shimadzu GC-2010 model equipped with a flame ionization detector and a Restek RTX-biodiesel column. The GC-MS analysis was carried out on a HP 5973 GC-MS equipped with a Restek 5-Amine column. NMR analysis was completed using an INOVA-600 equipped with a HC/N with XYZ-PFG probe.

5.3.2 Methods

The catalytic reactions were carried out under nitrogen in order to prevent air from reacting with the chloroaluminate and forming hydrochloric acid, which would then char the biomass before it could be properly solvated and catalyzed. The amount of soy flour biomass added was dependent upon the mass of chloroaluminate used and was reacted at concentrations of 3, 8, 10, and 20 mass/mass percent. The biomass was added in a one-pot batch and the mixture was reacted in a 90\textdegree C water bath for 2 hours under nitrogen with stirring at 150 RPM. The reaction mixture was then diluted with ethyl acetate and analyzed via GC, GC-MS and $^{13}$C-NMR.
5.4 Results

5.4.1 Experimental Data

It was found that using a concentration of 8% soy flakes (w/w) resulted in the highest production of the proposed dodecyl acrylate product. Interestingly, increasing the biomass concentration to just 10% caused an appreciable decrease in product yield, as can be seen in Figure 5-2 (p. 64). This is believed to be due as result of both mass transfer limitations and the inability of the chloroaluminate to effectively solvate the biomass when it is present in such high concentrations. The addition of a co-solvent, such as dichloromethane, may have been an effective solution to this issue, much like it was in the production of FAMEs in Chapter 4.

The figure also demonstrates that product conversion increased with time; at a much higher rate from 0 - 60 minutes, then slowing significantly after the first hour. This may be due to the existence of a mass transfer controlled region in the first hour, which then changes to one that is kinetically controlled for the remainder of the reaction.

Figure 5-2: The production of dodecyl acrylate based on biomass concentration (m/m), time, and temperature
5.4.2 Product Identification

As it was mentioned in Section 5.1, difficulty was experienced in correctly identifying the reaction product. The first step taken in determining the compound that was being extracted into the ethyl acetate was conducting GC-MS analysis. The results, which can be seen in Figure 5-3 (p. 65), show that the products of both the reaction and soy flour lipid extraction match very well.

Figure 5-3: (a) The representative reaction product is indicated as dodecyl acrylate (b) Results of the soy flour biomass, containing the same peak as the representative reaction (c) The dodecyl acrylate standard chromatograph matches the peaks of the other samples
The instrument provided an identification of dodecyl acrylate \((\text{C}_{15}\text{H}_{28}\text{O}_2)\), with 95% confidence; please refer to Appendix B Figure B-1 (p. 80) for the GC-MS identification of this compound.

A \(^{13}\text{C}\) NMR analysis was then run to further test the identification of the compound. The results are reported in Table 5-1 (66) and the NMR spectra can be found in Appendix B. Much like the GC-MS, the results demonstrate that the unidentified peaks within the representative reaction sample match those of the dodecyl acrylate standard and the predicted peaks obtained using the ACD Labs NMR predictor software. At this point, it was believed that the product was indeed dodecyl acrylate and therefore, the samples were analyzed using gas chromatography for quantification.

Table 5.1: \(^{13}\text{C}\) NMR Data Comparison for Proposed Dodecyl Acrylate Product

<table>
<thead>
<tr>
<th>Representative Reaction</th>
<th>Dodecyl Acrylate Standard</th>
<th>Predicted Dodecyl Acrylate</th>
</tr>
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<tr>
<td>EMIMCI Peaks (ppm)</td>
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<td>14.015</td>
<td>14.353</td>
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</table>

The final issue that allowed for the realization that the experiment was not proceeding as first believed was the fact that the dodecyl acrylate standard did not elute at the same time as the reaction product on the GC. The GC chromatographs in
Figure 5-4: (a) The dodecyl acrylate standard elutes at 9.8 minutes (b) The reaction product elutes at 23.9 minutes (c) The dodecyl acrylate standard chromatograph matches the peaks of the other samples

Figure 5-4 (p. 67) illustrate this problem very well; the reaction product elutes 14 minutes later than the product standard that was identified using GC-MS and NMR analysis. Therefore, it was concluded that the reaction product was identified incorrectly by the other methods, and furthermore, if the reaction did yield dodecyl acrylate, that it was not due to the reaction of the chloroaluminate with the biomass constituents, but rather that it was present in the soy flour itself.

5.5 Conclusions

The production of dodecyl acrylate from soy flour biomass using chloroaluminate ionic liquids was not accomplished, as it was determined that the supposed product was present in the unprocessed biomass itself. Nevertheless, the fact that acrylates are
indeed present within soy flour biomass may offer an opportunity for the generation of secondary value-added products in the industrial scale production of biodiesel. As can be seen in Figure 5-5, the importance of economically relevant by-products can not be understated in the overall process of becoming less dependent on non-renewable fossil fuels.

![Figure 5-5: The economic importance of producing valuable side products in the processing of biomass (*Self Approximated Values)*](image_url)
References


Appendix A

Additional Experimental Data
Obtained in the Study of the
Production of FAMEs using Lewis
Acidic Ionic Liquids
Figure A-1: (a) The elution times for mono, di and tri-glycerides are approximately 20, 27 and 33 minutes respectively. The lipid content of all samples was analyzed using a Restek RTX-Biodiesel Column (max. temp of 350°C) (b) The elution times for palmitic, linolenic, linoleic, oleic and stearic methyl esters. The methyl ester content of all samples was analyzed using an Agilent Durabond HP-88 column (max. temp of 250°C)
Figure A-2: The lipid standard curves as determined by GC analysis
Figure A-3: The FAME standard curves of as determined by GC analysis.
Figure A-4: (a) The GC-MS indicates that the sulfur compound is 1-(2-Thienyl)-1-propane (C$_7$H$_8$OS) with 49% confidence. The top component graph is indicative of the sample, while the bottom is from the NIST Library Software (b) GC-MS data indicates that the nitrogen compound is 4-amino-5-ethyloxycarbonyl (C$_6$H$_9$N$_3$O$_2$) with 38% confidence. The top graph is from the sample and the bottom is from the NIST Library Software
Figure A-5: (a) The six predicted peaks generated by ADC Labs NMR Software (b) Spectra of the EMIMCl standard from TCI America. The peaks at 77 ppm are due to the deuterated chloroform (c) Recovered EMIMCl spectra, the peaks at 77 ppm are chloroform-d.
Appendix B

Additional Experimental Data

Obtained in the Study of Dodecyl Acrylate Production
Figure B-1: (a) MS identification of the reaction product (b) NIST spectra for dodecyl acrylate. The two spectra match well and account for the 95% confidence reported by the instrument.
Figure B-2: (a) The predicted peaks generated by ADC Labs NMR Software (b) Spectra of the dodecyl acrylate standard from Polysciences, Inc. The peaks at 77 ppm are due to the deuterated chloroform (c) Reaction product spectra, the 77 ppm peaks are from chloroform-d.
Appendix C

Raw Data for the Production of FAMEs

Table C.1: Data for the three analyses of soy flour content. The triglyceride content present in soy flour correlates well among the three methods and agrees with common literature values (Liu, 1997)

<table>
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<tr>
<th>Sample</th>
<th>Triglyceride (m/m%)</th>
<th>FAME (m/m%)</th>
<th>TGA (m/m%)</th>
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<td>4</td>
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<td>21.74</td>
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<td>19.42</td>
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Table C.2: It was only possible to collect enough spent biomass for reactions that contained 15% solids or more by mass. This data allowed for the closure of the triglyceride carbon balance

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<th>FAME (m/m%)</th>
<th>TGA (m/m%)</th>
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<td>0.87</td>
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Table C.3: All reactions were run in 1.0 mL DCM and 1.0 mL MeOH at 90°C with approximately 205 mg solids for 4h

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Table C.4: All reactions were run in 1.0 mL MeOH and 0.1 mL IL at 90°C with approximately 330 mg solids for 4h

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Table C.5: All reactions were run in 1.0 mL DCM and 0.1 mL IL at 90°C with approximately 330 mg solids for 4h

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Table C.6: All reactions were run in 1.0 mL MeOH, 1.0 mL DCM, and 0.1 mL IL with approximately 330 mg solids

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<th>FAME (m/m%)</th>
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Table C.7: All reactions were run with 0.1 mL IL, 0.5 mL DCM, and 1.0 mL MeOH (optimized ratio) at 110°C

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<th>Biomass</th>
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