Purdue University
Purdue e-Pubs

Open Access Theses

Theses and Dissertations

January 2016

Corn Stover's Feasibility as a Biomass Feedstock Utilizing the "REACH" Process

Oskar James Kane
Purdue University

Recommended Citation

Kane, Oskar James, "Corn Stover's Feasibility as a Biomass Feedstock Utilizing the "REACH" Process" (2016). *Open Access Theses*. 1215.
https://docs.lib.purdue.edu/open_access_theses/1215

CORN STOVER'S FEASIBILITY AS A BIOMASS FEEDSTOCK UTILIZING THE "REACH" PROCESS

by

Oskar J. Kane

A Thesis

Submitted to the Faculty of Purdue University
In Partial Fulfillment of the Requirements for the degree of

Master of Science in Aviation and Aerospace Management

School of Aviation Technology
West Lafayette, Indiana
December 2016

THE PURDUE UNIVERSITY GRADUATE SCHOOL
STATEMENT OF THESIS APPROVAL

Dr. Gozdem Kilaz, Chair
School of Engineering Technology
Dr. Timothy Ropp
School of Aviation and Transportation Technology
Dr. Richard Fanjoy
School of Aviation and Transportation Technology

Approved by:
Dr. Richard Fanjoy
Head of the Departmental Graduate Program

To my grandfather, Sam…

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

5-MF	5-MethylFurfural
A-15w	Amberlyst-15 Wet
AirTIES	Air Transport Institute for Environmental Sustainability
ASTM	American Society for Testing and Materials
ATJ/SPK	Alcohol to Jet Synthesized Iso-Parafins
CAAFI	Commercial Aviation Alternative Fuels Initiative
CBE	Chemical and Biological Engineering
FAA	Federal Aviation Administration
FT	Fischer-Tropsch
GHG	Greenhouse Gas
HEFA	Hydro-Processed Esters and Fatty Acids
HPLC	High-Performance Liquid Chromatography
ICGA	Indiana Corn Growers Association
ICMC	Indiana Corn Marketing Council
LA	Levulinic Acid
LORRE	Laboratory of Renewable Resources Engineering
MSS	Multi-Sample Summary
OSHA	Occupational Safety and Health Administration
PCLP	Purdue University Crop/Livestock Linear Programming
PI	Principal Investigator
REACH	Renewable Acid-Hydrolysis Condensation Hydrotreating
RT	Retention Time
SIP	Synthesized Iso-Parafins
SPK	Synthesized Paraffinic Kerosene
SPK/A	Synthesized Paraffinic Kerosene plus Aromatics Derived from Alkylation
USDA	U.S. Department of Agriculture

ABSTRACT

Author: Kane, Oskar J. S. MS
Institution: Purdue University
Degree Received: December 2016
Title: Corn Stover’s Feasibility as a Biomass Feedstock Utilizing the “REACH” Process
Major Professor: Dr. Gozdem Kilaz

While there are currently five commercially allowed biofuel production processes via ASTM International Standard D7566, none of them consistently rely upon and utilize corn stover as a biomass feedstock source even though it is one of the most readily available domestic bio-resources. Mercurius Biofuels Inc.’s three-step Renewable Acid-Hydrolysis Condensation Hydrotreating process can convert virtually any biomass feedstock into jet fuel intermediates that are then blended with standard petroleum-based biojet diesel to create drop-in fuels.

The in-lab research backing this investigation was conducted to see if the second step of REACH, condensation, could be scaled further than the laboratory scale. Two set-ups were used for these experiments. Analysis of the in-lab research on condensation reactions focused on the conversion percentages of the two main components in the experiments, which were 5-Methylfurfural and Levulinic Acid. Experiments using both apparatus set-ups yielded successful conversions of these compounds. The in-lab research data analysis showed that the REACH process should be scaled past the laboratory level, and there exists potential for corn stover to serve as a biomass feedstock source for a sustainable fuels pathway that utilizes REACH.

CHAPTER 1. INTRODUCTION

Current petroleum-based jet fuels contribute to roughly 2-3% of all global carbon emissions, and the aviation industry is fully cognizant of this situation. Concurrently, as of 2012, national jet fuel usage has risen over 22 billion gallons annually and is forecasted to maintain or (most likely) increase that pace (Brown & Brown, 2012). Thus it is imperative that sustainable jet fuels are sought out to reduce the environmental impact of petroleum-based fuels. The challenge of manufacturing sustainable biofuels, however, is being able to produce them on a large, continuous scale, making the final product cost-competitive with petroleum-based fuels, and creating an eco-friendly product that will contribute significantly less greenhouse gas emissions (GHG) than standard aviation fuel.

Currently, American Society for Testing and Materials (ASTM) International standard D7566 permits five different biojet production processes for commercial and military use (ASTM Compass, 2016). The five ASTM International-approved methods are Fischer-Tropsch (FT) Hydroprocessed synthesized paraffinic kerosene (SPK), SPK from hydro-processed esters and fatty acids (HEFA), synthesized iso-parafins (SIP) from hydroprocessed fermented sugars, SPK plus “aromatics derived by alkylation of light aromatics from non-petroleum sources,” (SPK/A), and finally the newest method is called Alcohol to Jet (ATJ) SPK (ATJ-SPK) (ASTM Compass, 2016). These biofuel production methods use a variety of feedstock sources such as algae, camellia, sugarcane bagasse, and palm seed oils. However, none of those methods utilize corn stover as a source, regardless of the fact it is one of the most abundant domestic bio-resources that occurs as a by-product from another major industry (Brown & Brown, 2012).

1.1 Background of the Study

Mercurius Biorefining Inc. has developed a process, Renewable Acid-Hydrolysis Condensation Hydrotreating (REACH), for converting biomass feedstock to levulinate intermediates, from which jet fuels are produced (Mercurius Biorefining Inc., n.d., p. 1). The REACH process utilizes virtually any biomass; however, there is no current preference of feedstock selection for the REACH process. Mercurius partnered with Purdue University in 2013 to utilize REACH as an economically viable entity in the Midwest (Kilaz, Lopp & Mosier, 2015).

Mercurius and Purdue chose corn stover as the principal feedstock source because of its abundance in the region. Dr. Gozdem Kilaz, the principal investigator (PI) on this project, and her team commenced the research behind this investigation in August 2013 at Purdue University's Laboratory of Renewable Resources Engineering (LORRE). This study will be concluded in December 2016. Dr. Clay Wheeler (from the Chemical and Biological Engineering department at the University of Maine) provided Dr. Kilaz's team with assistance on the third and final step of the REACH process during 2016 by conducted hydrotreating experiments on the LORRE team's condensation experiment products.

1.2 Purpose and Objectives of the Study

The primary purpose of this investigation was to determine if corn stover is a feasible biomass feedstock source for a sustainable fuels pathway that utilizes the Mercurius REACH process. Compared to other feedstock sources, corn stover appears to meet the qualifications of a viable entity because of its abundance and relative cost-competitiveness. The in-lab research behind this investigation sought out to determine if corn stover could be scaled-up into an efficient, reliable and consistent feedstock source for a sustainable fuels pathway utilizing the REACH process.

The aspects examined were the accessibility and economic viability of corn stover, economic and ecological factors related to corn stover harvest, the current standard-approved biofuel production processes per ASTM International standard D7566, the comparison of corn stover to alternative biomass feedstocks, and the analysis of the LORRE team's experiments using the condensation stages of the REACH process.

1.3 Research Question

Is corn stover a feasible biomass feedstock source for a sustainable biofuels pathway that utilizes the Renewable Acid-Hydrolysis Condensation Hydrotreating process?

1.4 Significance of the Study

The aviation industry's vast and growing demand for jet fuel justifies the need for alternative and renewable fuel production processes that are sustainable (economically, socially, and environmentally) and have high accessibility to feedstock sources. The findings of this investigation will contribute to the benefit of the biofuel production industry, as the feedstock costs are crucial parameters that determine the success of any biorefinery. In Indiana, there is the advantage of great experience in farming that results in abundant amounts of corn stover per each harvest season.

Although ASTM International standard D7566 currently permits five available processes for biojet production, only one of their feedstock sources (algae) rival the accessibility and energy output of corn stover (Brown & Brown, 2012; ASTM Compass, 2016). If deemed feasible for commercial production, Mercurius, additional REACH technology investors, biofuel manufacturing companies, and investing corn farmers will all mutually benefit from a corn stover to jet fuel development procedure utilizing REACH. Because of stover's abundance and high profit margin, corn farmers will be encouraged to ration their corn stover surplus to balance the maintenance of their fields and crops and the demands of their operational costs with the supplying of local jet fuel production plants.

1.5 Assumptions of the Study

The current study assumed that:

1. The Mercurius patented REACH process is a reliable and efficient method both in terms of economic, chemical and ecological factors.
2. The analysis techniques utilized by the high-performance liquid chromatography (HPLC) system are accurate and reliable.

1.6 Limitations of the Study

The limitations of the current study are:

1. The reactor size for both the hydrolysis and condensation experiments is a 1-liter bench vessel. Due to Occupational Safety and Health Administration (OSHA) regulations, these reactions need to be executed under an operating hood, which places a maximum limit on the reactor size.
2. The in-lab research for this investigation will testify specifically to corn stover's ability to be scaled up to a large batch reaction utilizing REACH. The economic analysis of corn stover and comparison to other ASTM International standard

D7566-approved biofuel production processes are based solely on research through a literature review.

1.7 Delimitations of the Study

The delimitations of the current study are:

1. Dr. Kilaz and peers working on this project decided upon the specific chemicals and their respective amounts used in experiments.
2. Dr. Kilaz and peers prepared the base structure of the acid hydrolysis and condensation experimental setups.
3. Only two catalyst types were utilized in the reaction system. There is a chance to investigate added options, but the time frame requires keeping the scope manageable.

1.8 Definitions

Biojet: In this investigation, the term *biojet* is used to mean any clean fuel that is derived from a biomass feedstock source, manufactured through ASTM International Standard D7566-approved processes, and is an environmentally friendly alternative to common, petroleum-based fuels (International Air Transport Association, 2012, p.6).

Biomass Feedstock: The dictionary definitions of the terms *biomass* and *feedstock* are “plant materials and animal waste used especially as a source for fuel” and “raw material supplied to a machine or processing plant.” In this investigation, the term *biomass feedstock* is used to mean, “Plant materials that serve as a source and are treated for fuel production processes,” (Biomass, n.d; Feedstock, n.d.).

Drop-In Jet Fuel Blends: The Commercial Aviation Alternative Fuels Initiative (CAAFI) defines *drop-in jet fuel blends* as “a substitute for conventional jet fuel… (And) a drop-in fuel blend does not require adaption of the aircraft/engine fuel system or the fuel distribution network, and can be used ‘as is’ on currently flying turbine-powered aircraft,” (Drop-In Jet Fuel Blend - CAAFI, 2016).

Feasibility as a Biomass Feedstock: In this investigation, the term *feasibility as a biomass feedstock* refers to the potential of corn stover to be utilized as a source for a sustainable biofuels pathway. Corn stover would be deemed a feasible feedstock if it can be successfully scaled-up through the levels of the REACH process and if there exists a sufficiently large total land area to produce enough stover that would supply a significant portion of the aviation industry’s fuel consumption demands.

Fuels Pathway: In this investigation, the term *fuels pathway* is used to mean any process that converts a biomass feedstock source to drop-in jet and diesel biofuels (Kilaz, Lopp & Mosier, 2015, p.1).

Sustainable: In this investigation, the term *sustainable* is used to mean a process or thing that is environmentally friendly, helps to reduce the global carbon footprint, and can be relied upon for consistent use based on economic parameters (Kilaz, Lopp & Mosier, 2015, p.1).

1.9 Summary

In summary, the current research study was focused on investigating the feasibility of corn stover as a biomass feedstock source for a sustainable biofuel pathway that utilizes Mercurius’ patented REACH process. This chapter provided an introduction into the necessity for sustainable biofuel pathways, and how Mercurius, their technology, and their collaborative work with researchers at Purdue University fit into the scope of current commercial biojet production. The next chapter contains an overview of the existing literature related to the necessity for aviation biofuels as well as the advantages of corn stover economically, agriculturally, and ecologically. A separate section in the next chapter contains a description of how Mercurius and Purdue’s research ties into corn stover usage. The third chapter provides the methodology behind experimental setups and procedures used during Dr. Kilaz’s team’s experiments, as well as measures for experimental success and potential threats to experimental validity. The fourth chapter presents and analyzes the data and in-lab findings of this research. The fifth chapter presents the major point of and concludes this investigation.

CHAPTER 2. REVIEW OF LITERATURE

The purpose of the current study was to identify economic and ecological factors related to corn stover harvest, to compare corn stover to alternative biomass feedstocks used in commercial production of jet fuel, and to investigate whether corn stover is a feasible feedstock source for a sustainable fuels pathway utilizing the REACH process. In order to better understand these factors and demonstrate gaps in the existing knowledge base, a review of the literature was conducted.

2.1 The Need for Biofuels

The U.S. Energy Information Administration found that petroleum-based fuels accounted for approximately 82% of national energy consumption in 2009 (Thompson & Tyner, 2011). One major problem is a large quantity of this fuel is imported. “In 2015, the United States imported approximately 9.4 million barrels per day (MMb/d) of petroleum from about 82 countries,” (U.S. Energy Information Administration, 2016b, p.1). For perspective, 9.4 MMb/d equates to 3.43 billion barrels of imported petroleum in 2015. There are geo-political, environmental, economic, and strategic reasons for the United States to produce its own domestic transportation fuels (Kilaz, Lopp & Simmons, 2014). Energy independence provides many fortunate advantages.

A Federal Aviation Administration (FAA) emission primer (2005) reported that all aviation activity contributes to roughly 2.7% of the United States’ entire greenhouse gas (GHG) emissions. However, the aviation industry is continuously growing at a rapid pace. Thus a demand exists for eco-friendly, sustainable transportation fuels, which offer similar or better performance and cost-competitiveness than petroleum-based fuels. The aviation industry recognizes this situation, and many different organizations have already undergone efforts to produce biojet fuel. Currently there are five processes available for commercial biojet production per ASTM International standard D7566. Though a handful of those methods' feedstock sources rival the energy output, none rival the accessibility and abundance of corn stover (Clarens, Resurreccion, White & Colosi, 2009).

2.2 Cellulosic Biomass Production

The main feedstocks in this investigation contain a material called cellulosic biomass, which can be converted into valuable biofuels. Specifically, the substance cellulosic ethanol duplicates the chemical structure of petroleum-based fuel such as gasoline and diesel (Brown & Brown, 2012). Recently, the U.S. Department of Agriculture (USDA) for the first time sponsored a plant that sustainably harvests biomass feedstocks for cellulosic-ethanol production. As of late 2014, the plant, formally known as the DuPont Cellulosic Ethanol facility "is expected to generate over 30 million gallons annually of biofuel produced from corn stover" (Doran, 2014, p. 2). Additionally, the same facility along with Iowa State University's BioCentury Research Farm conducted studies for more than two years to determine the ratio of corn stover that should be harvested compared to corn stover that should be left on the fields. Their team found that five days after corn stover was partially removed from the fields, 20 percent of crops sprouted faster rather than being hindered, and they also found that one month after planting, they had similar or better numbers of crops than the farmers expected (Doran, 2014). This implies that if the farmers desire exceptional crop productivity, it is vital that they harvest the excess corn stover from their fields.

2.3 Farmers' Results

Brown and Brown (2012) report that corn stover is the largest available agricultural residue in the United States. As of mid-2014, farmers in central Iowa produced around five tons per acre of corn stover on average, whereas they needed only two and one-half tons per acre to protect and prevent erosion of the soil (Doran, 2014). On average, the farmers acquired about two and one-half tons of excess corn stover per acre, but according to them, this created problems when left unattended. The central-Iowan farmers described the problem of excess stover in their own words: "It interferes with crop establishment and early growth for the next crop, immobilizes nitrogen and harbors crop pathogens" (Doran, 2014, p. 1). Therefore, leaving the large amounts of stover on the fields creates further problems during future harvests, and so, if farmers wish to have healthy produce and reach expected or greater numbers during harvest, they must remove the excess corn stover from their fields. The results from this study also correlate with the DuPont Cellulosic Ethanol facility and the BioCentury Research farm's findings towards the leftover stover. Not only does the excess stover harm the health of the produce, it also negatively affects the overall yield.

2.4 Economics of Corn Stover

Edwards (2014b) states that the average cost of harvesting and transporting stover is $24.35 per bale, and the average minimum price a farmer would accept from a buyer is $29.27 per bale. Therefore, on average, a farmer makes a minimum of $5.00 per bale. If a typical bale weighs 1,200 pounds or 0.6 tons, then five dollars per pale of profit equates to $8.33 profit per ton of corn stover (Edwards, 2014b).

For example, if the central-Iowan farmers from Section 2.3 followed this theoretical model, they would make a profit of $20.83 for every 2.5 tons of excess stover per acre. Today, most farms producing corn on a commercial scale are quite large; often their acreage is greater than 200. Macdonald, Korb and Hoppe (2013) reported that the average acreage for corn farms was 600 in 2007. Thus, by following the same model, a 600-acre farm in central-Iowa would earn $12,500 in profits from excess stover sales during a harvest season. Even if a farmer in this example didn’t sell the full 2.5 tons of excess material per acre, he or she could still make a sizable profit. Not only is it important for excess stover to be removed post-harvest for the health of the fields and high crop yields, but also selling the excess stover can make a strong addition to a farmer’s profits per harvest season.

The price of corn stover per ton, however, depends on the quality of bale content. When stover sits on the fields, it collects moisture and ash, which varies per four independent variables: “…Soil type, weather patterns, harvest method and storage techniques” (Thompson & Tyner, 2011, p. 3). Ash is described as the dust and crop debris collected on the stover and bale during the harvest process. If the stover contains high enough levels of moisture and ash, a penalty is deducted from the overall cost of the bale.

2.5 Penalties Due to Poor Bale Quality

Thompson and Tyner (2011) used the Purdue University Crop/Livestock Linear Programming (PCLP) model to simulate yields of corn stover and their costs. “With data provided by farmers on land, labor, machinery, crop yields, crop prices, input costs, and other farm resources, PCLP determines the most profitable combination of crops to grow and the optimal acreage devoted to those crops" (Thompson & Tyner, 2011). The PCLP model used 25 farms, or a total of 63,582 acres, for its analysis, which altogether served as a representative of Midwest crop farms. Thus the PCLP model's results are a fairly good estimate of farm behavior. Then, Thompson and Tyner (2011) used the model to create a system for deducting a penalty from the overall worth of the stover based on the levels of moisture and ash.

Bales containing less than 20% moisture and 10% ash would not be penalized, and this type of bale made up approximately 61.44% of model simulations. Bales that were between 20 and 28% moisture and 10 and 15% ash were penalized $8.00 per ton, and bales between 28 and 36% moisture and 10 and 15% ash were penalized $17.00 per ton. Those bales accounted for 29.20% and 0.83% of the model simulations, respectively. If the bale contained over 36% moisture and 15% ash, it was considered unusable and worthless, and these bales accounted for 8.52% of the model simulations (Thompson & Tyner, 2011). Farmers have a genuine stake in preserving their stover surplus by removing it soon after crop harvest because the longer they wait, the greater the potential exists for their bales to collect moisture and ash. After collecting the excess corn stover, farmers must decide how they want to use or profit from it. At this point, there exists a potential for establishing a surplus source of corn stover to serve as a biomass feedstock for a sustainable fuels pathway.

2.6 Usage of Corn Stover

Although corn stover is such an abundant and available material, its uses are limited. Aside from its usage in biofuel production and soil protection, corn stover is utilized as bedding for larger livestock and as a low quality, reserve livestock feed

(Pennington, 2013). However these secondary uses require very little stover compared to the overall quantity of stover surplus. While corn stover affects the food production industry indirectly by helping to insulate or preserve moisture in fields of crops, corn stover does not affect the food production industry directly whatsoever. This means a large quantity of excess stover remains even after its other uses have been accomplished. Concurrently, there is a dire need for sustainable biofuel pathways in the entire transportation industry. If corn stover proved to be a viable source for biofuel creation, its main use would be as a biomass feedstock for biojet production processes. This is because producers would continuously want to make biofuel using the substantial available quantities of stover.

2.7 Comparison to Algae

A major step in determining corn stover's feasibility as a biomass source is comparing its chemical properties to other feedstocks. Clarens, Resurreccion, White and Colosi (2009) compared algae, corn, canola and switchgrass to determine their energy outputs. Only algae and corn will be discussed further, because they are the leading candidates for a viable biofuel feedstock. Canola and switchgrass produced considerably lower levels of energy than either algae or corn, and their cultivation is much more difficult as well

Algae produced significantly higher energy levels than corn (seven and a half times greater) however its cultivation used significantly more water than corn's (almost 15 times greater). Remarkably, the cultivation of algae created more levels of GHG emissions than it consumed, 1.8 +/- 0.58 kg CO_2 per one unit functional unit of energy of algae; whereas cultivation of corn produced a positive net GHG consumption, -2.6 +/-

0.09 kg CO_2 per one functional unit of energy of corn (Clarens et al., 2009). For comparison, standard jet fuel produces 70.90 kg CO_2 per million British thermal units (Btu) (U.S. Energy Information Administration, 2016a, p.1). Therefore, the production of corn in and of itself consumes GHG while production of algae outputs GHG. In an attempt to create sustainable biofuel pathways, this is an important fact to consider when deliberating between potential feedstock sources.

Algae is beneficial in the sense that it requires approximately three times less land than corn for cultivation. "The land use estimates indicate that algae cultivation on roughly 13% of the United States' land area could meet the nation's total annual energy consumption. In contrast, use of corn would require 41% of total land area," (Clarens et al., 2009, p. 3). For reference, 41% of the United States' landmass is greater than the total area east of the Mississippi River. However, that statistic reflects the amount of land area required for either algae or corn stover that would supply the entire aviation industry's fuel demands. As of 2015, cornfield covered 88.9 million acres of landmass in the United States (U.S. Department of Agriculture, 2015). The United States is approximately 2.3 billion acres large, with Alaska accounting for 375 million acres (Wuerthner, 2002). Thus there are approximately 1.9 billion acres of land in the contiguous United States. This means that existing cornfields and cornfield infrastructure cover approximately 4.68% of all of the United States' landmass, and that there is slightly over 10% of total landmass already in existence that would be required for corn stover to supply the aviation industry's total fuel demands. Thus corn stover can still potentially contribute a significant portion of the total fuel supply needs of the aviation industry.

The difference between corn stover and algae, however, is that a large amount of infrastructure for corn cultivation is already in existence. Every corn harvest season, large amounts of stover is collected as a byproduct, which means it is acquired regardless of if the initial intention of growing corn was for creating a biofuel feedstock. This differs from algae, which would have to be grown specifically for the purpose of making a biofuel feedstock. Algae can be used as fertilizer and in dietary supplements, however its overall uses aren't nearly as impactful as corn's because corn is a major staple of the food production industry. This means that using algae as a feedstock source for a potential sustainable biofuel pathway would require creating many farms to support the surplus of algae. Alternatively, the foundation for growing and collecting corn stover is already in place in the form of crop fields across the country.

2.8 ICMC, Mercurius and Purdue

Mercurius Biofuels Inc. and the Indiana Corn Marketing Council (ICMC) partnered with Purdue University to collaborate on joint investigations concerning sustainable aviation fuels. "Collaboration between the industry (Mercurius), academia (Purdue University), and government (Indiana Corn Growers Association) will provide the expertise necessary for the optimal utilization of Indiana's corn for a great cause of clean energy" (Kilaz et al., 2014, p. 3).

In 2014, the ICMC bestowed a grant to Dr. Kilaz's team to establish the most cost efficient and effective means of preliminary corn stover preparation for input to the REACH process (Kilaz et al., 2015). The ICMC, which comprises of 17 directors with various farming experience and backgrounds, is tasked with managing and investing state corn checkoff funds, which are supplied from corn producers who seek further research and investigation, into programs that bolster the Indiana corn industry (Indiana Corn Marketing Council, 2016). The ICMC is interested in maximizing the total profit of corn stover sales as well as optimizing the process and reducing the cost of the feedstock's preparation for Indiana's farmers. It should be noted that ICMC is a branch of the Indiana Corn Growers Association (ICGA). The ICGA works to improve Indiana farmers' profits by serving as, "… The voice in local, state, and national legislature, judicial and regulatory agencies' decisions affecting agriculture," (Indiana Corn Growers Association, 2016). The ICMC has provided invaluable government expertise to the research team since 2014.

As an aligning organization for Dr. Kilaz's research team, Mercurius Biofuels Inc. has contributed the necessary industry expertise for a thorough investigation. Mercurius' mission is to, "… produce a wide range of products from nutraceutical and other chemicals to profitable drop-in fuel through a process of novel applications of existing technologies," (Mercurius Biorefining Inc., 2016, p. 1). Partnered with the (former) Aviation Technology Department's Air Transport Institute for Environmental Sustainability (AirTIES) Research Center at Purdue, Mercurius received a $4.6 million cost share grant to develop corn stover into military grade jet fuels utilizing their newly developed REACH process (Kilaz et al., 2014). Mercurius and Purdue's AirTIES Center have a contract to develop the REACH process as an economically viable commercial entity in the Midwest region of the United States. Mercurius believes their REACH process can fully utilize corn stover's potential as a feedstock source, and they recognize the vast abundance and availability of the material in the Midwest region. The underlying research for this investigation commenced in August 2013 (Kilaz, Lopp & Mosier, 2015).

2.9 REACH Process Overview

The REACH process utilizes any feedstock that contains cellulosic biomass and is insensitive towards impurities in the feedstock because it does not use any enzymes or microbes (Mercurius Biorefining Inc., n.d., p. 1). This means that REACH will still produce the same quality of biojet fuel regardless of the level of ash and moisture residing on the corn stover. Keep in mind hardly any other feedstocks rival the abundance and availability of corn stover.

The resulting products from REACH are blended with traditional aviation fuels to produce drop-in fuels (Mercurius Biorefining Inc., n.d, p.1). The term drop-in refers to a specification that any new alternative fuel undergoing ASTM International testing must be able to be used in existing aircraft without any structural or powerplant changes needing to be made. Byproducts of REACH include potentially high valuable chemicals, which are still being investigated.

The process itself is appealing. “The process is significantly faster than many other biofuel production methods, has lower capital and operating expenses, and does not rely on food crops for feedstock,” (Mercurius Biorefining Inc., n.d, p.1). Compared to the current ASTM International Standard D7566-approved biofuel production processes, a great potential exists for REACH to become a sustainable fuels pathway utilizing corn stover as a feedstock.

2.9.1 Three stages of REACH

The REACH process comprises of three stages: Acid-hydrolysis, condensation and hydrotreating. Mercurius Biofuels Inc. provides an outline of the underlying chemistry and technology behind REACH on their website, as depicted in Figure 2.1.

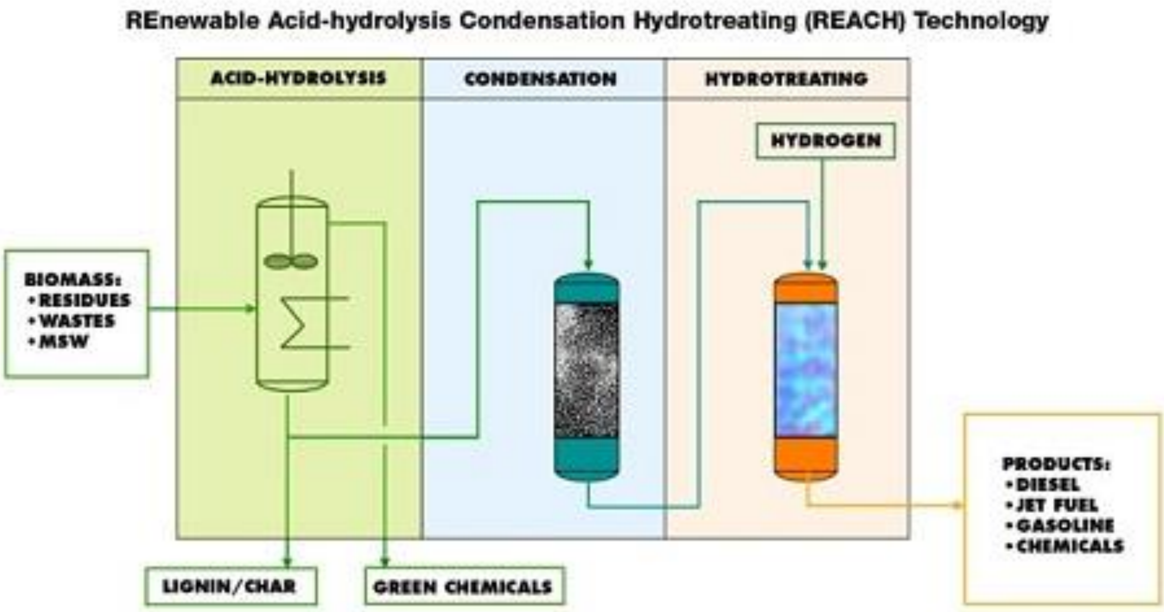


Figure 2.1 The REACH process' three stages: Acid-Hydrolysis, Condensation, and Hydrotreating (Mercurius Biorefining Inc., n.d.).

"The first step in the REACH process is to treat non-food biomass in an acid hydrolysis unit to create a mixture of non-sugar intermediates in high yields," (Mercurius Biorefining Inc., n.d.). For this investigation, forage chopped samples of corn stover served as biomass in the acid-hydrolysis step. The corn stover was provided by New Holland Farm in Rochester, Indiana, as well as by Purdue University's farms.

In the second step, the non-sugar intermediates are processed into usable carbon chains through the utilization of a condensation reaction (Mercurius Biorefining Inc., n.d, p. 1). This is, “A reaction in which two or more reactants yield a single main product with accompanying formation of water and some other molecule,” (IUPAC Gold Book, 2014). This stage of the REACH process utilizes high temperatures and a condensation tube that filters the reaction with cool water.

The final step of the REACH process, hydrotreating, is crucial to producing a drop-in aviation jet fuel. This step must yield a product that mimics that same type of chemical structure as observed in petroleum-based fuels. Petroleum-based fuels are made up of many types of hydrocarbon chains differing in length. The final products of REACH accumulate a large quantity of their carbon from the acid-hydrolysis of the biomass feedstock and the majority of their hydrogen from the hydrotreating of condensation products. Hydrotreating is a reaction where the intermediate products resulting from the condensation stage of REACH are deoxygenated and hydrogenated to form usable hydrocarbon fuel chains (Mercurius Biorefining Inc., n.d, p. 1). This means any remaining oxygen atoms are removed as best possible from the compound, and hydrogen is entered into the system to form with the carbon into hydrocarbon chains.

2.10 Conclusion

In order to produce investigative results for the research question posed, a literature review was conducted. There exists a great necessity for sustainable biofuel pathways that combat GHG emissions and produce as much energy as and combat the cost-effectiveness of petroleum-based fuels. Although commercial production of biojet has been occurring for the past three-quarters of the decade, none currently utilize corn stover as a feedstock source. This is surprising because corn stover is perhaps the most abundant domestic bio-resource available (Brown & Brown, 2012).

The purpose of the current study was to identify economic and ecological factors related to corn stover harvest, to compare corn stover to alternative biomass feedstocks used in commercial production of jet fuel, and to investigate whether corn stover is a feasible feedstock source for a sustainable fuels pathway utilizing the REACH process. In order to better understand these factors and demonstrate gaps in the existing knowledge base, a review of the literature was conducted. The information necessary to answer these questions has been addressed in the literature review and is contained within the results of Chapter 4. The experimental methodology is discussed in detail in the next chapter.

CHAPTER 3. METHODOLOGY

This research focused on investigating the feasibility of corn stover as a feedstock source for a sustainable biofuels pathway utilizing the REACH process. There are many steps required to establish a sustainable fuels pathway, which include, but are not limited to, testing the fuel's characteristics for certain degrees of performance such as stability, lubricity, fluidity and viscosity (ASTM Compass). However, one necessary step for establishing a sustainable fuels pathway is securing a reliable, consistent, and efficient method that converts biomass into drop-in bio-diesel and jet fuels.

To test if a proposed method is reliable and efficient, scale-up reactions must be performed. Scale-up reactions are a series of experiments that all operate with the same testing conditions. However, the total amount of reacted components is increased during each trial. For example, the process has to prove that it can successfully produce 500 milliliters (mL) of biofuel products, then it must be able to produce one liter of products, followed by 5 liters, and so on and so forth.

This research specifically analyzed the chemical makeup of products throughout the condensation stage of the REACH process. The main measure of success for the research team's analysis was if greater than 50% conversion of 5-methylfurfural (5-MF) and 20% conversion of levulinic acid (LA), the two main ingredients in the condensation reactions, was achieved. 5-MF and LA were selected based on previously determined standards and confidential experimental procedures from Mercurius. An additional measure of success was if the new condensate products formed. The research team primarily used a HPLC system for analysis purposes. The in-lab research was aimed to see if corn stover could successfully be scaled up through the REACH process at the small-batch laboratory scale.

3.1 Hypothesis

This investigation's hypothesis is as follows: Corn stover should prove to be a feasible biomass feedstock for a sustainable fuels pathway by utilizing Mercurius' REACH process. Stover is the major byproduct of corn harvest, and in recent years, farmers are accumulating abundant quantities of excess stover (Doran, 2014). REACH is an efficient process and operates with a fair amount of ease (Mercurius Biorefining Inc., n.d.).

Although it may be unrealistic that the cost of producing biofuels made from REACH (with corn-stover as the feedstock) may not directly beat out the cost of producing petroleum-based fuels, but should stay within the relative price range. Corn stover's abundance and ease of manufacture via the REACH process places it in an elite category among potential feedstock sources for sustainable biofuel pathways. Although it is unrealistic to expect corn stover could supply the total fuel quantity demands of the aviation industry, corn stover can however contribute a significant portion to international jet fuel needs.

3.2 LORRE Condensation Reaction Setup Details

A heating device is required to incite and drive the second stage of the REACH process. During condensation reactions, the LORRE team utilized both a standard water bath and a jacketed vessel reactor attached to a heating system. The following subsections will outline the details of each apparatus set-up.

3.2.1 Standard Water Bath

From November 2015 to August 2016, the LORRE team utilized the standard water bath for condensation experiments. During these trials, the water bath was heated to 75 degrees Celsius (° C), which was the maximum temperature limit for the specific model of water bath in use. This temperature limit would later prove to be the cause for seeking out a new, alternative heating system. Figure 3.1 depicts the standard water bath setup during condensation reactions.

Figure 3.1 Standard water bath apparatus setup for condensation experiments conducted in LORRE.

Within the water bath, a one-liter, open, cylindrical Pyrex glass container was used to enclose the compounds. Aluminum foil, plastic wrap, or some other type of wrapping material was used to cover up the remaining open area of the water bath. This prevented the water inside the bath from evaporating during the 24-hour long reaction. An impeller attached to a roto-motor was stabilized to a vertical bar and placed so the impeller was positioned only a few centimeters above the center and bottom of the cylinder. The impeller was turned on for the duration of the reaction so that it would properly blend and stir the components within the container.

A rubber stopper was used to plug the opening of the glass container enclosing the compounds. The rubber stopper had three holes, and the first two holes were used for lowering the impeller into the container and attaching the condenser tube. The third hole was required for the researcher to lower a long pipet down and inside the container to take samples. All three openings were lubricated with gear grease because large amounts of pressure would build up during the reaction.

A standard condensing tube fixed with two rubber hoses was fitted into the rubber stopper, which can be observed in Figure 3.1. The water faucet was turned on for the duration of every reaction regardless of other conditions. When the faucet was turned on, water flowed from the faucet through the first hose to the bottom opening of the condenser, up the sleeve of the tube, out the upper opening of the condenser to the second hose, and down to the drain to leave the system. The purpose of the condenser was to filter the reaction with hydrogen and oxygen molecules in the form of cool, running water as well as to prevent any condensation products inside the glass cylinder from evaporating and leaving the system. As heated gases travel up the condenser, they turn to back liquids from the filtering water and fall down into the container. The condensation tube is employed in the jacketed vessel reactor experiments as well.

3.2.1.1 Standard Water Bath – Testing Conditions

The standard experimental run consisted of 150 mL of 5-MF and LA being added to the glass cylinder along with 20.52 grams (g) of Amberlyst-15 wet (A15w) resin, which served as the catalyst for the reaction. A15w was selected based on previously determined standards and confidential experimental procedures from Mercurius. Essentially, the A15w helps ions move between the 5-MF and LA. There were additional experiments that reacted 275 mL of 5-MF and LA and 37.62 g of A15w, and these were performed with the intention of producing large quantities of condensation products to ship to Dr. Wheeler, CBE - University of Maine, for hydrotreating.

First the water bath was heated to its max temperature of 75° C. The impeller was turned to a setting of 4 out of 10 (approximately 80 revolutions per minute [rpm]) and remained spinning for the duration of the experiment. These experiments were conducted for 24 hour-long trials. Table 3.1 outlines both experimental procedures utilized with the standard water bath.

Table 3.1

Comparison of Standard Water Bath Reactions

5-MF : LA Ratio	Amberlyst-15w Amount	Water Bath Temperature	Total Reaction Time	Impeller Setting
150 mL : 150 mL	20.52 g	75° C	24 hours	4-6/10
275 mL : 275 mL	37.62 g	75° C	24 hours	4-6/10

After the full 24 hour-run was complete, the water bath, impeller, and water for the condensation tube were turned off. The final condensation products were a non-viscous liquid substance, and they were moved to a separate container, which was either dark or clear and subsequently covered with aluminum foil. The bottles were then labeled appropriately and moved to a freezer. The remaining products comprising of A15w resin and small traces of 5-MF and LA were soaked with distilled water, moved to a separate container, and stored in a freezer. This was done because the resin is quite expensive and conveniently can be cleaned and preserved.

Between five and ten samples were taken from the condensation reaction at specific time intervals during the 24-hour duration of the experiment, and samples at time equal to zero (T=0h), 12 hours (T=12h), and 24 hours (T=24h) were always collected. After taking each sample, they were labeled with the time from when the reaction began (i.e. T=0h, 12h, etc.) the experimenter's initials, and the date. The samples were stored in an appropriately labeled container and kept inside a freezer.

Additionally after the full 24 hour-run, the samples were processed through an HPLC system to detect the specific levels of LA, 5-MF, and other traces of compounds. The HPLC system compared the results from the samples to a set of standards that were conducted in December 2015 and February 2016. The standards were created from the results of the analysis of two sets containing five condensation trials each. These standards would then represent expected levels of LA and 5-MF for each future sample trial. From this point on, anytime a HPLC analysis of a condensate product sample was executed, the sample's results were automatically compared against these pre-determined standards.

3.2.2 Jacketed Vessel Reactor and Heating Unit System

The LORRE research team switched to a system comprising of a jacketed vessel reactor fixed to a heating unit for condensation reactions in October 2016. The team made the decision to switch reactors because the new heating unit possessed a much higher temperature range. This was because this type of technology was not available previously when the research team was utilizing the standard water bath. A jacketed vessel reactor contains a thin sleeve that surrounds the main inner chamber. Heated liquids flow through the sleeve, which thereby heats the vessel and any reacting compounds. Figure 3.2 displays the LORRE team's jacketed vessel reactor.

Figure 3.2 Jacketed vessel reactor apparatus setup for condensation reactions conducted in LORRE.

The LORRE research team utilized propylene glycol as the liquid to flow through the sleeve of the jacketed vessel reactor. Propylene glycol was used because its boiling point is 188.2° C, which is far beyond the temperature requirements needed for the condensation reactions. The green liquid in Figure 3.2 is the propylene glycol residing in the sleeve, and the heating unit can be observed to the right of the jacketed vessel reactor in the image.

Just like during the standard water bath condensation experiments, a condenser tube fixed with two rubber hoses was fitted to the jacketed vessel reactor, which can be observed in Figure 3.2. The water faucet was turned on for the duration of every reaction. The hoses were attached in the same fashion as previously, so that water would flow from the faucet through the bottom hole of the condenser, up the tube, out the upper hole of the condenser, and down the drain. Furthermore, the jacketed vessel reactor also contained an impeller that was used to stir and blend the components. The impeller was lowered into the inner chamber of the jacketed vessel reactor and would run for the duration of every reaction regardless of any other conditions.

The jacketed vessel reactor experiments were heated to 75 and 120° C. The reasoning behind running a reaction at 75° C with the jacketed reactor was to replicate the experiments performed with the standard water bath. The results from both set-ups performing a condensation reaction at 75° C were analyzed and compared to observe any potential differences in the two reactors.

3.2.2.1 Jacketed Vessel Reactor - Testing Conditions and Procedures

First, the faucet was turned on so water would flow through the condenser tube and down the drain. Then the heating unit was activated, and either 75 or 120° C was entered on the heating unit's display monitor. While waiting for the heating unit to rise to the desired temperature, the A15w was weighed out and the 5-MF and LA were set out for use. After the heating system achieved the desired temperature, the impeller was activated, and the LA was added to the inner chamber of the jacketed vessel reactor, followed by the A15w, and lastly the 5-MF. The components were added in this order due to their physical natures. 5-MF and LA are liquids, and A15w is bead-shaped, adhesive, and smaller than the thickness of a grain of rice. The A15w often left small remnants around the walls of the jacketed vessel reactor’s opening and throughout the inner chamber. Thus by adding the components in the order they did, the LORRE research team cleanly washed the remaining A15w resin stuck to the sides of the reactor’s opening and inner chamber with 5-MF and LA.

During the condensation experiments with the jacketed vessel reactor, a one to one ratio for 5-MF and LA served as the standard amount of components to be used. The one exception is that in November 2016, the LORRE research team investigated a two to one ratio of 5-MF to LA. However, even when following a one or two to one ratio for 5-MF to LA, experiments rarely followed the standard amount of ingredients to be used, which was 100 mL of 5-MF and LA and 13.68 g of A15w. There were a few reasons for this; one being that on a few different occasions, there was a shortage of one of the components so 100 mL of both 5-MF and LA could not be reacted. Furthermore, the total reaction time and impeller setting varied throughout the series of experiments. These parameters changed so that the LORRE research team could observe any potential significant changes in the total conversion percentages of 5-MF and LA. Table 3.2 displays the various condensation reaction procedures utilized with the jacketed vessel reactor.

After the full 24- (or 36) hour reaction was completed, the heating unit, impeller, and water faucet were all turned off. The condensation reaction products were then emptied through the bottom of the jacketed vessel reactor into a large glass container.

The products were allowed to settle for five minutes, and following, the condensation products were collected in an amber-colored glass container and removed from the remaining soaked A15w resin. Just like during the standard water bath condensation reactions, the remaining resin was washed with distilled water and moved to a separate container. Both the condensate products and remaining resin were labeled appropriately and stored in the freezer.

Table 3.2

Comparison of Jacketed Vessel Reactor Experiments

5-MF : LA Ratio	Total Amberlyst-15w Amount	Water Bath Temperature	Total Reaction Time	Impeller Setting	Double Catalyst (Yes or No?)
100 mL : 100 mL	13.68 g	120° C	24 hours	4.5/10	No
87 mL : 87 mL	11.902 g	120° C	36 hours	5.5/10	No
91 mL : 91 mL	12.45 g	75° C	24 hours	6/10	No
200 mL : 100 mL	41.04 g	120° C	24 hours	8/10	Yes
400 mL : 200 mL	82.08 g	120° C	24 hours	8/10	Yes

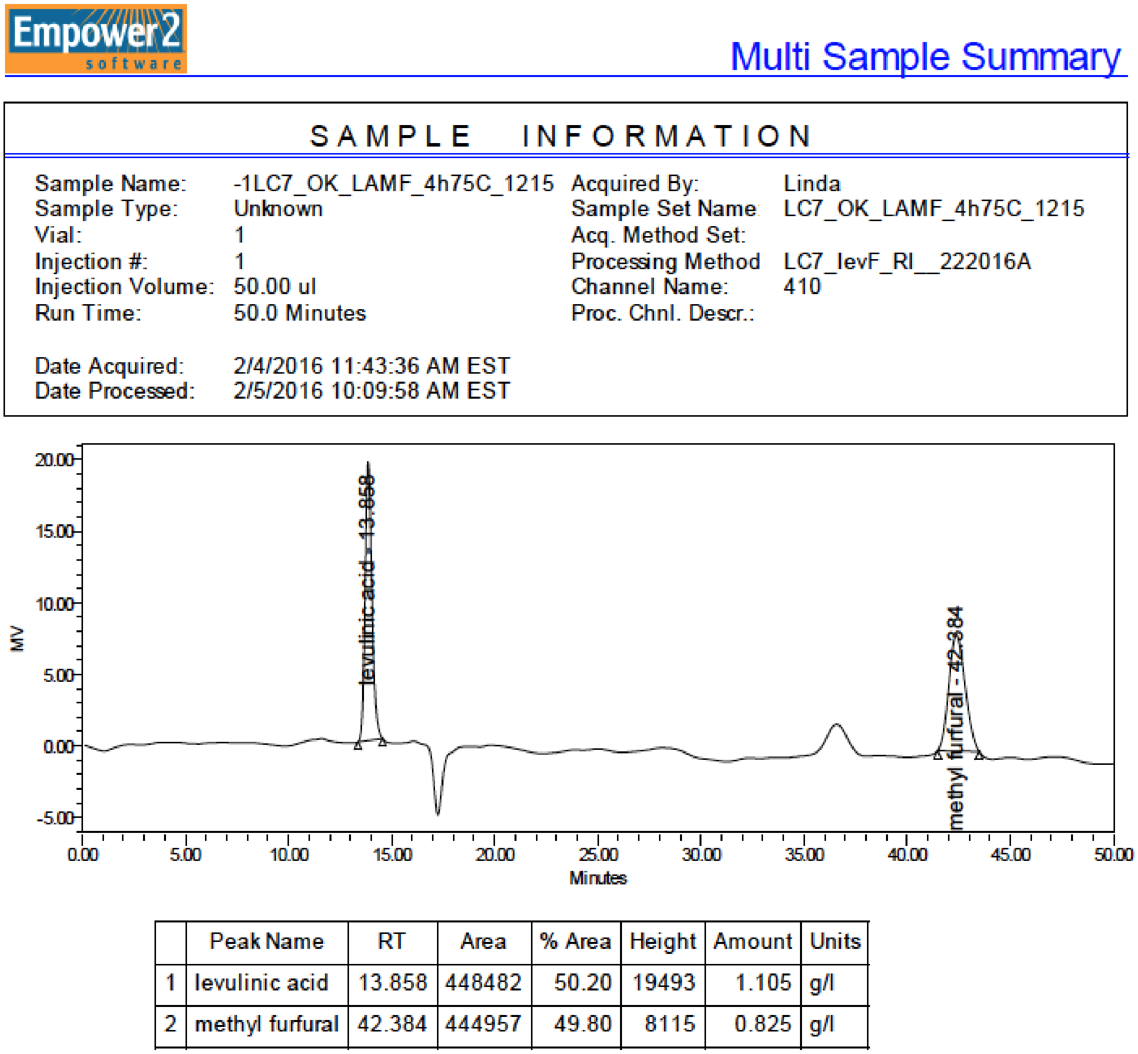
Like the trials with a standard water bath, samples were taken at various times throughout the duration of the jacketed vessel reactor experiments. Samples were always taken at the beginning, middle, and end of every reaction, and they were stored in the freezer. The samples were then analyzed in an HPLC system and processed with the same pre-determined standards as from the standard water bath experiments. HPLC was a crucial tool for the LORRE research team by calculating the amounts of each compound throughout the reaction.

3.3 High Performance Liquid Chromatography Analysis Overview

Upon conducting a HPLC analysis, a multi-sample summary (MSS) of the data is produced; see Figure 3.3. The MSS includes the sample's name, set name, the HPLC processing method, the data acquiring and processing time, the HPLC run time, the vial number, the injection number and volume, a graph of the compounds' peaks, and a breakdown of the summary's graphical statistics.

The vial number refers to the specific placement of each vial within the HPLC machine (our machine can hold over 100 vials). The injection number refers to the frequency of trials from each vial; for instance a vial could have three separate injection trials. Every HPLC trial discussed in this write-up was run for 50.00 minutes with one injection per sample and an injection volume of 10.00 micro-liters (µl).

In Figure 3.3, the graphical summary reports the retention time (RT) (x-axis) for each compound's peak in minutes. The retention time is the time it takes a compound to travel through the column and be detected by the HPLC's detector, measured from injection to detection (Clark, 2007). The y-axis, megavolts (MV), represents the strength of the detected compound, which correlates to the area under the curve and the volume. The area under the curve of each compounds' peak allows the determination of the amount or volume of each compound, which is the most important piece of information for this research. The amount of each compound in any given sample is measured in g/l or mg/ml. The amount of each compound is important because ultimately we seek to find how much LA and 5-MF is consumed during the condensation process.


Empower2 software

Multi Sample Summary

SAMPLE INFORMATION

Sample Name: -1LC7_OK_LAMF_4h75C_1215
Sample Type: Unknown
Vial: 1
Injection #: 1
Injection Volume: 50.00 ul
Run Time: 50.0 Minutes

Date Acquired: 2/4/2016 11:43:36 AM EST
Date Processed: 2/5/2016 10:09:58 AM EST

Acquired By: Linda
Sample Set Name: LC7_OK_LAMF_4h75C_1215
Acq. Method Set:
Processing Method: LC7_levF_RI__222016A
Channel Name: 410
Proc. Chnl. Descr.:

	Peak Name	RT	Area	% Area	Height	Amount	Units
1	levulinic acid	13.858	448482	50.20	19493	1.105	g/l
2	methyl furfural	42.384	444957	49.80	8115	0.825	g/l

Figure 3.3 HPLC MSS of condensation reaction products.

For the rest of this investigative report, only the graphs of the compound’s peaks will be displayed from the MSS’s. Otherwise, the MSS’s will take up too much space with unnecessary information such as, for example, the channel number or processing set name. Additional tables in Chapter 4 will display the amount of each compound in a sample along with other data.

3.4 Specific Measures of Success

After conducting HPLC analyses with the samples, a successful measure occurs when greater than 50% of 5-MF and 20% of LA is converted. This means the final sample of a condensation reaction must contain 50% or lower 5-MF and 80% or lower LA from the initial volume of each compound for it to be considered successful. These two percentages were determined based off of Mercurius', Dr. Kilaz' and LORRE peers' guidelines. High conversion percentages are important because it means the components are reacting and forming the new condensate products. Also, the hydrotreating phase of REACH does not operate at full efficiency if leftover 5-MF remains in the condensation products. It is expected that the levels of compounds are similar to or match those founds in the previously conducted standards. In the experiments conducted in the Spring and Fall 2016, The LORRE research team sought to achieve greater than 50% 5-MF and 20% LA conversion during condensation experiments.

3.5 Threats to Validity

The most common threat to validity in this experiment occurs through the setup. On more than once occasion, condensation experiments were discarded because errors in the setup occurred such as the heat or impeller turning off during operation. Additionally, liquid levels in the standard water bath diminished due to evaporation. Another possible threat to validity is that if the HPLC standards conducted in 2015 were not completely accurate, any further samples taken and compared to those standards would not be not accurate representations of the desired levels of LA and 5-MF.

3.6 Summary

From February to May and August to December 2016, this investigative research study employed two primary set-ups for the condensation reactions of the REACH process: A standard water bath and a jacketed vessel reactor. Results from both reactors were analyzed and processed using an HPLC system. The HPLC output an analysis from which the conversion percentages of 5-MF and LA could be calculated. Subtracting the final amount (at T=24 or T=36) of a compound from its initial amount (T=0) and dividing the result by the initial amount results in the conversion percentage of that compound. These results will be presented and discussed in detail in Chapter 4.

CHAPTER 4. PRESENTATION OF DATA AND RESULTS

The focus of this investigation was to determine the feasibility of corn stover as a feedstock source for a sustainable biofuels pathway utilizing the three-step REACH process. Since this investigation commenced in February 2016, Dr. Kilaz's LORRE research team has only conducted in-lab research on the second step of REACH: The condensation reaction. The quantitative in-lab research described in this investigation involves the measurement of the levels (in g/L) of two specific compounds, 5-MF and LA, over the course of a condensation reaction. A LORRE HPLC system was used to analyze products from the reaction and measure the levels of 5-MF and LA at each sample. The results from those analyses are presented in this chapter.

4.1 MSS's of Condensation Reactions and Conversions of Products

The LORRE research team utilized two set-ups during their trials with condensation reactions. The first was a standard water bath reactor and the second was a jacketed vessel reactor. In the following two subsections, two MSS's (at time equal to zero [T=0h] and at the end of the reaction [T=24h]) from each apparatus setup are presented. MSS's from the T=0h and T=24h (or T=36h) sample allow the user to measure the conversion percentages of each compound. The procedure for this type of measurement and the conversion percentages of 5-MF and LA coming from the two sets of MSS's will be presented later in this section.

4.1.1 Standard Water Bath – MSS's

HPLC analyses from the condensation experiments (utilizing a standard water bath) were mainly performed in March and April 2016. The standard procedure for these experiments consisted of the following steps: First the water bath was turned to 75° C;

then the faucet was turned on so that cool water would flow through the condensation tube; next, 150 mL of 5-MF and LA, and 20.52 g of A15w catalyst resin were added to the container, the impeller was set to 4/10, and finally the container was sealed for the duration of the 24-hour reaction with the exception of the times that researchers would take samples.

After concluding a condensation reaction, all of the samples were prepared and loaded into a LORRE HPLC system for analysis. The HPLC analyses were processed against a set of pre-determined standards, which then output a MSS, which is a page of statistics. The piece of data most important to this investigation coming from the MSS is the volume or amount of each compound at any given sample. The graphs from two MSS's collected in March 2016 show the differences in volume of 5-MF, LA, and other various compounds from start to the end of the reaction; see Figures 4.1 and 4.2.

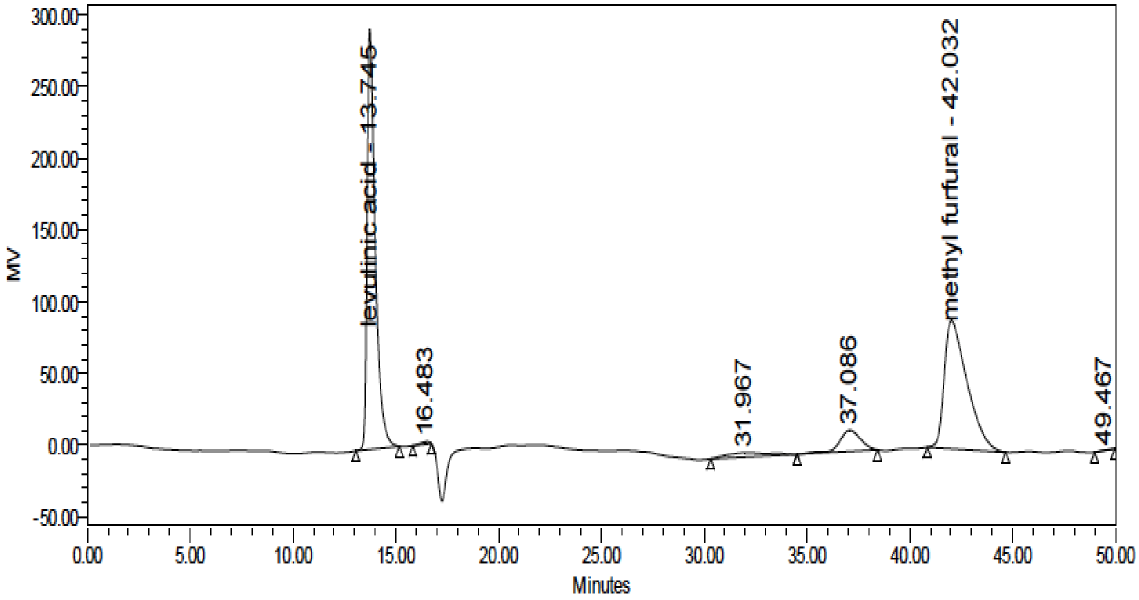


Figure 4.1 MSS of Condensation Reaction utilizing standard water bath at T=0.

Upon first observation of each figure, there is a lack of variation between each levulinic acid peak, which is the peak that occurs at around 14 minutes. However, the y-axis is scaled two times greater in Figure 4.1 than Figure 4.2 due to the HPLC system's processing method. For example, the LA peak at T=24 is only roughly 170 MV large, whereas the LA peak at T=0h is approximately 290 MV. Fortunately the HPLC processing method calculates the MV values of each compound into amounts (in g/L), but one can still observe that there is less LA present at T=24h than there was at T=0h. This means that the missing LA was consumed during the condensation reaction.

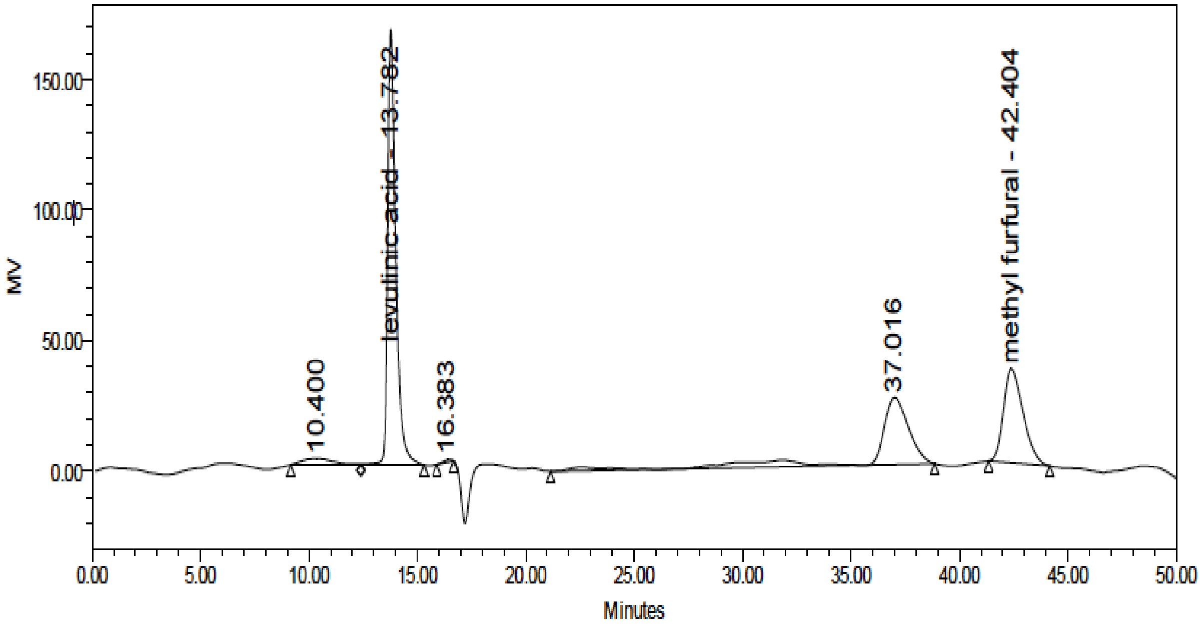


Figure 4.2 MSS of Condensation Reaction utilizing standard water bath at T=24

An additional important note is the small-to-medium sized peak at around 37 minutes to the left of the 5-MF peak. The LORRE research team believes this is the peak of the new, desired condensate product. Throughout the condensation experiments, the research team always noted if the new condensate products ever grew to a significant or large amount. However at the time of this investigation's completion, no significant new condensate products were ever observed. In the following subsection, the conversion percentages of 5-MF and LA from the MSS that contained Figure 4.1 and 4.2 are presented.

In Section 4.2, tables containing all of the condensation reaction's conversion percentages will be presented.

4.1.1.1 Standard Water Bath – Conversions of 5-MF and LA

As Figures 4.1 and 4.2 show, the volume of 5-MF and LA lessens between T=0h and T=24h. This is because during the 24-hour reaction, 5-MF and LA react together to form new additional compounds. The measures of success for the in-lab research backing this investigation was to achieve greater than 50% conversion of 5-MF and 20% conversion of LA over the course of a full reaction. Table 4.1 displays the conversion percentages of 5-MF and LA from Figures 4.1 and 4.2.

Table 4.1

Standard Water Bath Condensation Reaction – 3/29/16

Sample Time	Peak Name	RT	Amount (g/L)	Converted %
T0	5-MF	42.032	11.028	66.44%
T24	5-MF	42.292	3.701	
T0	LA	13.745	18.917	42.85%
T24	LA	13.782	10.182	

To calculate the conversion percentages of each compound, the T24 amount is subtracted from the T0 amount and the result is divided by the T0 amount. The resulting number represents how much of the compound was consumed during the reaction. For example, to determine the conversion percentage of 5-MF from Figures 4.1 and 4.2, the T24 amount, 3.701, is subtracted from the T0 amount, 11.028, which equates to 7.327. This number is then divided by T0 (11.028), and the answer, 0.6644 represents the total amount of 5-MF that is no longer present in total mixture of compounds.

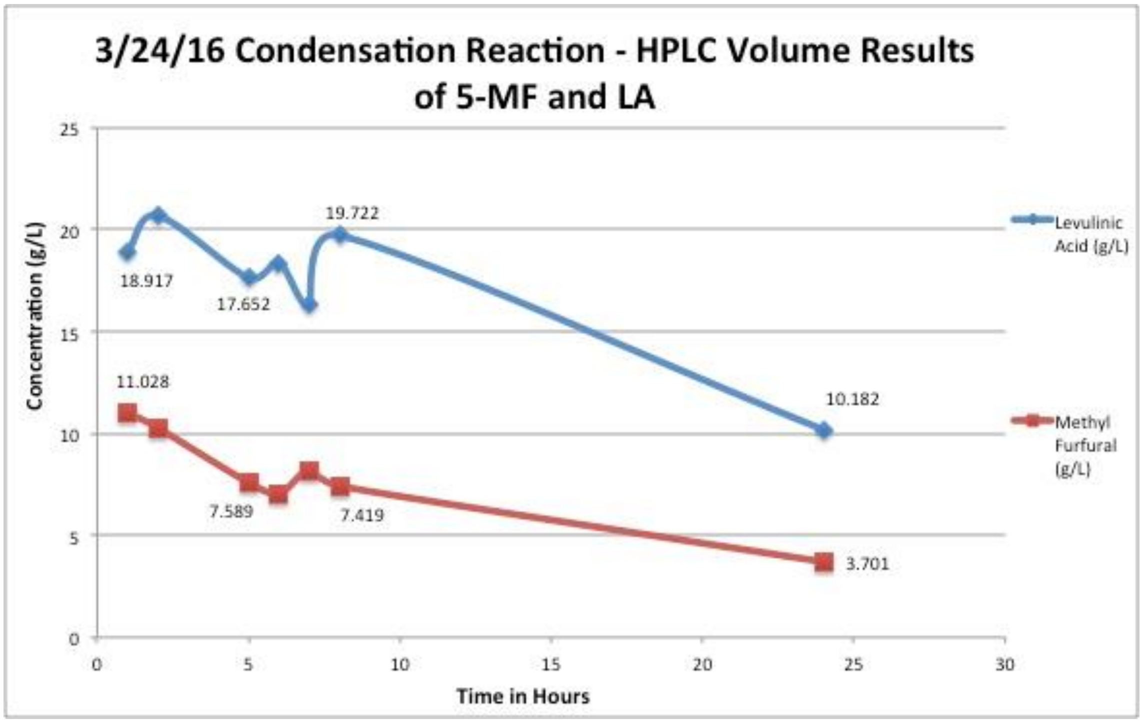


Figure 4.3 Change in volume of 5-MF and LA throughout a standard water bath condensation reaction.

As shown in Table 4.1, the conversion percentages of both 5-MF and LA are above their corresponding measures of success for this in-lab research. In this March 2016 reaction, 5-MF was converted 66.44% and LA was converted 42.85%, which means both compounds exceeded their 50% and 20% measures of success, respectively. Figure

4.3 displays the overall trend in each component’s consumption throughout the same condensation reaction backing Table 4.1.

4.1.2 Jacketed Vessel Reactor – MSS’s

HPLC analyses from the condensation experiments (utilizing the jacketed vessel reactor) were performed from September to December 2016. The jacketed vessel reactor nearly followed an identical methodology as the standard water bath. The procedure for these experiments consisted of the following steps: First the heating unit was activated and set to the desired temperature; then the faucet was turned on so cool water flowed through the condensation tube; next, either a one or two to one ratio of 5-MF to LA and the appropriate amount of A15w catalyst resin were added to the container, the impeller was turned on to the desired setting, and the container was sealed for the duration of the 24-hour reaction with the exception of the times researchers took samples.

After the condensation reaction concluded, the samples were prepared and loaded into a LORRE HPLC system for analysis. The HPLC analyses were processed against the same pre-determined standards as previously referred to in this investigation, and in return would provide a MSS. MSS’s contains various data about the condensation reaction samples, and the statistic most valuable to this investigation is the volume or amount of each compound in a sample. Two graphs from a MSS collected in October 2016 show the difference in volume of 5-MF, LA, and other various compounds from start to the end of the jacketed vessel reactor condensation experiment; see Figures 4.4 and 4.5.

The condensation experiment from which this MSS resulted was heated to 120° C, contained 100 mL of both 5-MF and LA as well as 13.68 grams of A15w resin, and reacted for 24 hours.

While not as noticeable as from the examples presented in Section 4.1.1, the y-axis of Figure 4.4 is scaled slightly larger than in Figure 4.5. For example, the LA peak at T=24h is around 280 MV, whereas the LA peak at T=0h is around 330 MV. Fortunately the HPLC system processes and calculates the MV values of each compound into amounts (in g/L), and one can still observe that there is less LA present at T=24h than there was at T=0h. This means that the missing LA was consumed during the condensation reaction, and the same is observed for 5-MF.

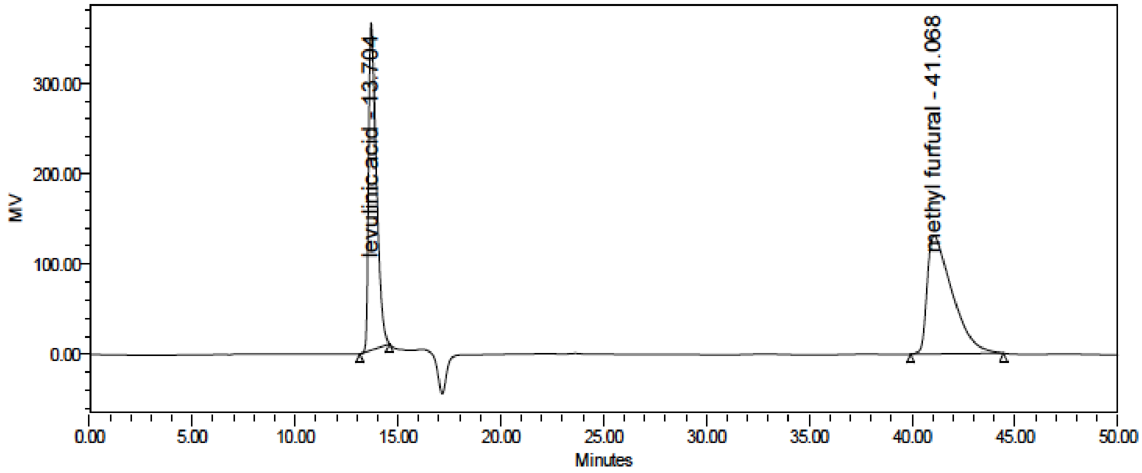


Figure 4.4 MSS of Condensation Experiment utilizing jacketed vessel reactor at T=0.

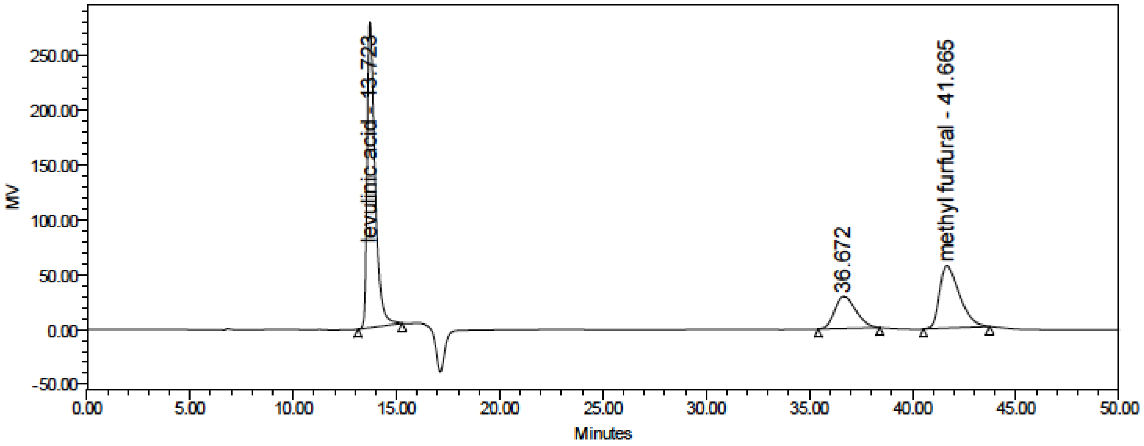


Figure 4.5 MSS of Condensation Experiment utilizing jacketed vessel reactor at T=24.

An additional observation is the formation of the new condensate products to the left of 5-MF at 36.67 minutes in Figure 4.5. In Figure 4.4, this peak is not present, which leads to the notion that this new condensate product was formed during the reaction. The size of this peak, while not significantly large, is important because it confirms that the 5-MF and LA are reacting together to form additional compounds. This is an important measure of success for small, laboratory batch-sized reactions especially in the overall process of scaling up a sustainable biofuel production method. The appearance and formation of the new condensate product means there is a solid ground for Mercurius to continue testing condensation reactions to search for the optimum conditions that result in the complete conversions of all compounds. The LORRE research team is performing some of these tests by continuing to research the optimum conditions for the condensation reactions, however said research was ongoing by the time this investigation concluded. In the following subsection, the conversion percentages of 5-MF and LA from the MSS that contained Figure 4.4 and 4.5 are presented.

4.1.2.1 Jacketed Vessel Reactor – Conversions of 5-MF and LA

The method for calculating the conversion percentages of each chemical followed the same structure as outlined in Section 4.1.1.1. Table 4.2 displays the conversion percentages of 5-MF and LA from the MSS that contains Figures 4.4 and 4.5.

In this October 2016 condensation reaction, 5-MF was converted 64.98% and LA was converted 22.17% in relation to their 50% and 20% measures of success, respectively. The conversion percentages of both 5-MF and LA are above their corresponding measures of success for the condensation experiments. Additionally, Figure 4.6 displays the overall trend of each component's consumption throughout the condensation reaction. It can be observed that typically, the largest amount of consumption takes place within the first eight hours.

Table 4.2

Jacketed Vessel Reactor Condensation Experiment – 10/14/16

Sample Time	Peak Name	RT	Amount (g/L)	Converted %
T0	5-MF	41.068	17.612	64.98%
T24	5-MF	41.665	6.167	
T0	LA	13.704	22.641	22.17%
T24	LA	13.723	17.622	

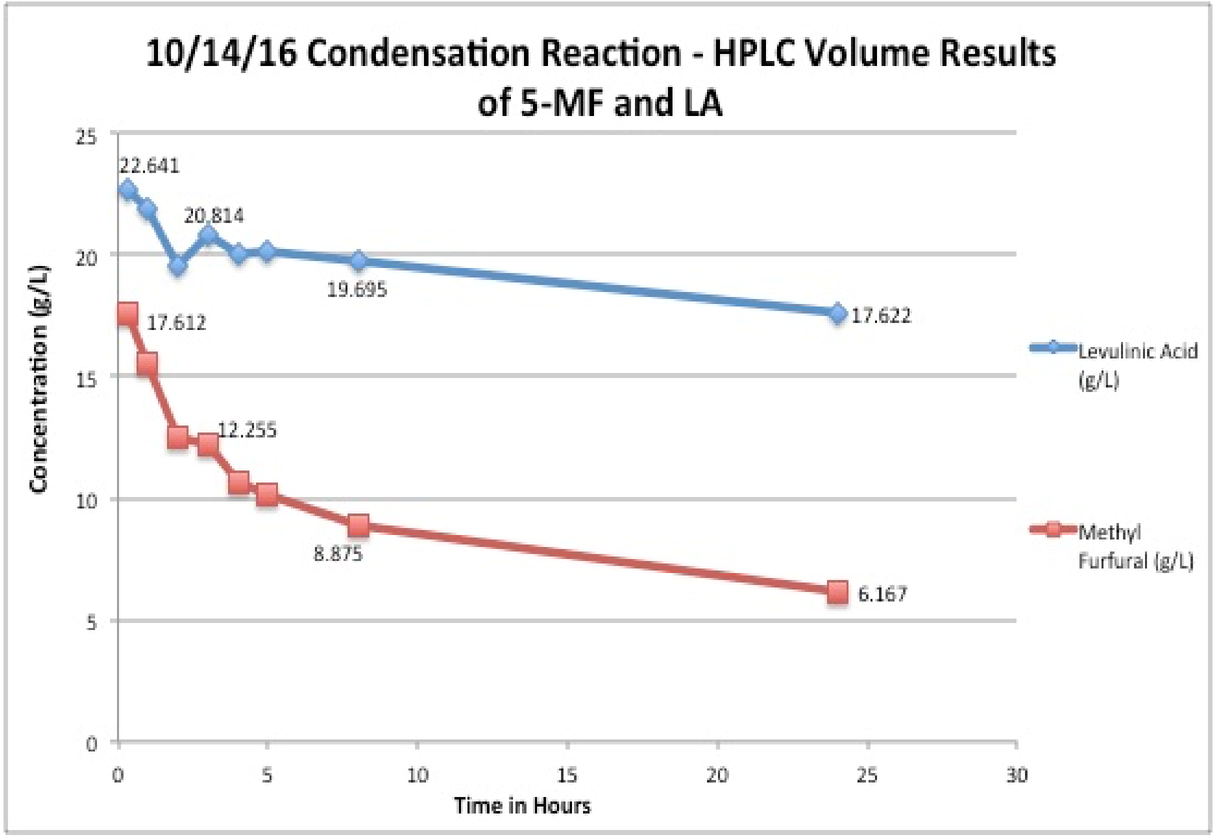


Figure 4.6 Change in volume of 5-MF and LA throughout a jacketed vessel reactor condensation experiment.

The LORRE research team inferred that possibly the components were reacting with the A15w catalyst early on in the reaction, then ceased as time goes by. So the research team attempted condensation experiments with double the normal dosage of catalyst. In these reactions, the same amount of A15w that was added at T=0h was added to T=12h as well. The double-catalyst reactions were outlined briefly in Table 3.2, however the following section will discuss these results in more detail. The next section will also compare the conversion percentages of 5-MF and LA from all condensation experiments.

4.2 Conversions of 5-MF and LA – Final Results from All Condensation Experiments

During the active period of this investigation, over 15 condensation experiments were conducted either with the standard water bath or the jacketed vessel reactor. However, not every experiment received HPLC analysis. Sometimes because of equipment failure, procedural error, or unexpected results, not every reaction was able to have HPLC analysis performed on their respective samples. Furthermore, some condensation reactions were conducted with the intention of not performing HPLC analysis. This often occurred when creating large batches of condensation products for hydrotreating at the University of Maine, which would have followed the successful HPLC results of a previous trial reaction.

Out of all the condensation experiments performed during this investigation, five separate reactions functioned without any discrepancies and operated with the intention of receiving HPLC analysis. Table 4.3 presents these five reactions and their respective conversion percentages. The header on the first column in Table 4.3 is meant to label each of the five reactions to provide ease in discussion throughout the remainder of this investigation. The header on the second column represents the standard water bath (SWB) or jacketed vessel reactor (JVR). Each conversion percentage was calculated with the same procedure as described in Section 4.1.1.1. For the sake of space conservation, the volumes of 5-MF and LA at T=0h and T=24h (or T=36h) hours were left out of Table 4.3. The conversion percentage of each compound delivers the same message in a more concise manner.

Table 4.3

Condensation Experiments and the Conversion Percentages of 5-MF and LA

Trial #	SWB or JVR	Date	5-MF:LA Conversion % at T=24 hours	5-MF:LA Amount and Ratio (mL)	Double Catalyst (Yes or No)	Water Bath or Unit Temp.	Total Reaction Time
1	SWB	3/24-24/2016	66.44% : 42.85%	150 : 150	No	75° C	24 Hours
2	JVR	10/13-14/2016	64.98% : 22.17%	100 : 100	No	120° C	24 Hours
3	JVR	10/18-19/2016	64.63% : 19.64% (at T=36 hours)	87 : 87	No	120° C	36 Hours
4	JVR	11/3-4/2016	38.57% : 16.29%	91 : 91	No	75° C	24 Hours
5	JVR	11/8-9/2016	42.78% : 23.99%	200 : 100	Yes	120° C	24 Hours

4.3 Major Takeaways – Final Results from All Condensation Experiments

As observed in Table 4.3, both of the reactions that were void of a successful 5-MF conversion (trials 4 and 5) were within 12% of 5-MF's measure of success, and both of the reactions that did not contain a successful LA conversion (trials 3 and 4) were within 4% of LA's measure of success. Therefore when these condensations reactions did not meet 5-MF or LA's measure of success for conversion, the result was still within proximity of success.

In three of the condensation reactions (trials 1, 2, and 3), 5-MF was consumed as much as 14% more than its measure of success for conversion, and one of the experiments (trial 1) yielded slightly higher than 22% above LA's measure of success for conversion. Though, it is key that with all three of these condensation reactions, the measure of success for both 5-MF and LA was attained twice and once, trial 3, only barely missed its measure of success for LA. Trials 2 and 3 were performed at 120° C in the jacketed vessel reactor and trial 1 at 75° C in the water bath, as well as trials 1 and 2 lasting for 24 hours and trial 3 for 36. This means that although these three reactions differed from each other by temperature, run-time, or apparatus set-up, they all achieved highly successful measures of success for conversion of 5-MF, and two achieved successful measures of LA while the third, trial 3, fell short by a small amount.

Only one reaction that utilized the standard water bath received a complete HPLC analysis, trial 1. However, this experiment followed a number of trial-and-error reactions that were performed and either malfunctioned or did not correctly complete reacting. Each previous experiment was meant to fine-tune the overall process in order to hopefully achieve higher conversions of 5-MF and LA, and those trials would prove to be quite useful. This is because the standard water bath condensation reaction shown in Table 4.3 recorded the highest conversion percentages for both 5-MF, 66.44%, and LA, 42.85%, out of all the other presented experiments. This is interesting because it means there exists further potential for testing condensation reactions with the standard water bath's procedure but scaled one degree larger.

It is also interesting to note that the only other experiment presented in Table 4.3 that was heated to 75° C, trial 4, also recorded the lowest two conversions of 5-MF and

LA out of all five condensation reactions. However, this is most likely because the jacketed vessel reactor had a tendency to collect A15w particles at the bottom of the inner chamber, which was shaped like a funnel and thereby prevented the resin from properly flowing and interacting throughout the inner chamber of the reactor. When the reaction was performed at 120° C, the particles appeared to mix better in the inner chamber than if the temperature was set to 75° C. In the standard water bath, the container has a flat, round bottom and thus there were no crevices for the A15w to accumulate and stop flowing. Ultimately, the standard water bath's container shape served to be the major positive point that it held over the jacketed vessel reactor, whereas the latter proved to be more user-friendly in terms of activating and maintaining the heat and possessing a much higher temperature capacity.

Only one reaction that was run for 36 hours, trial 3, received a complete HPLC analysis, and that experiment achieved its measure of success for 5-MF but fell slightly short of LA's. It should be noted that this 36-hour jacketed vessel reactor condensation experiment converted 64.63% of 5-MF, which was similar to results coming from 24-hour long reactions. This means that even though the reaction operated for 50% longer time than standard procedures, it converted approximately the same amount of 5-MF as reactions performed for 24-hours. The LORRE research team concluded that 36-hour long reactions were not necessary to continue performing because they did not yield significant increases in conversions of 5-MF and LA compared to 24-hour long reactions.

As a final note on Table 4.3, the only reaction listed that utilized the double catalyst procedure also achieved the second highest conversion of LA among all five experiments, 23.99%; however it fell short of 5-MF's standard for success by slightly more than seven percent. The double catalyst procedure was used because the LORRE research team felt that perhaps some of the A15w was being burned up due to the high temperatures of the jacketed vessel reactor condensation experiments. Therefore by adding an additional batch of A15w halfway through the reaction, the components would receive a fresh batch of catalyst to further convert 5-MF and LA. As of 17 November 2016, the research team is continuing to study the double catalyst procedure. Two other full reactions have been completed at this point, but the problem is that the T=24h sample for each of these trials was not processed correctly. This is because the sample contains compounds that are not received well in the HPLC system. Therefore the LORRE research team is investigating how to properly prepare the T=24h sample for HPLC analysis. At this time, results from the double catalyst look promising but a definitive conclusion cannot be made.

4.4 Summary of Data Findings and Results

In order to measure whether the condensation stage of the REACH process could successfully be scaled-up through small-batch laboratory reactions, the current investigation studied the volume of individual components throughout an experiment to observe decreasing amounts of the compounds over time. The LORRE research team conducted condensation experiments with two differing set-ups: a standard water bath and the jacketed vessel reactor fixed to a heating unit system. Following a condensation reaction, the products would be stored away into a freezer, and the samples taken throughout the experiment would be prepared for analysis.

This research team utilized a HPLC system to analyze the condensation reaction samples, and after performing an analysis, a MSS was collected. The MSS contained a variety of data, but most importantly it included the volume (in g/L) of compounds in the sample. The volume of two of the three ingredients for the condensation experiment, 5-MF and LA, were tracked throughout condensation reactions to observe the conversion or consumption percentage. The theory is that as the components react during the experiment, they contribute their own molecules together to form a new condensate product, which decreases the total amount of both 5-MF and LA. If the volume of 5-MF at T=0h is 20 g/L and its volume at T=24h is 10 g/L, then the compound was converted 50% over the course of the reaction. This investigation set its measures of success to be greater than or equal to 50% conversion for 5-MF and greater than or equal to 20% conversion of LA. This means a successful reaction would have achieved greater than 50% consumption of 5-MF and 20% consumption of LA throughout its duration.

Out of five completed condensation reactions that were devoid of any procedural errors or equipment malfunction, four achieved at least one of the measures of success and two achieved both. When performed correctly, there exists great potential for condensation reactions to be scaled-up. If the reactions rose above the laboratory scale, the set-ups at the next level would most likely adopt industry-approved reactors. Reactions performed for 36 hours did not yield more significant results than 24-hour long reactions, so the 24-hour reaction was set as the norm run-time. The LORRE research team is still currently investigating double-catalyst batch condensation reactions, although the results so far look promising. Single-catalyst batch, condensation experiments performed for 24 hours at 75° C in the standard water bath and 120° C in the jacketed vessel reactor proved to be the most effective procedures for converting both 5-MF and LA.

Chapter five will summarize this investigation’s purpose, research question, literature review, methodology, data and in-lab research results, and the final recommendation stemming from this overall body of work.

CHAPTER 5. SUMMARY, CONCLUSION AND RECOMENDATIONS

The research question posed by this investigation involved the feasibility of corn stover becoming a feedstock source for a sustainable biofuels pathway that utilizes Mercurius Biorefining Inc.'s three-step REACH process. The in-lab research backing this investigation sought out the scale-up potential and examined the conversion efficiency of the second step of REACH, condensation. HPLC analysis was used to examine and determine the conversion efficiency of condensation reaction products. Specifically, the HPLC system measured the consumption trend of the two primary reactants, 5-MF and LA, over the course of a condensation experiment.

This last chapter reviews the aims, summary, and findings of this study as well as presenting recommendations for future investigations into scaling-up the REACH process.

5.1 Aims of the Study

Currently, the aviation industry is making great strides towards utilizing sustainable, eco-friendly fuels in commercial and military applications, and there are even five commercially allowed biofuel production processes per ASTM International Standard D7566. However none of these methods primarily and consistently utilize corn stover as a feedstock source, however this research is underway in numerous organizations in the U.S. (ASTM Compass, 2016). Mercurius selected corn stover because it is rarely used in other biofuel production processes and is widely available in the Midwest United States (Brown & Brown, 2012).

This research investigation sought out if corn stover could prove to be a feasible biomass feedstock source for a sustainable fuels pathway that utilizes REACH. There are three main factors that determine feasibility. First, the final fuel product of REACH would need to be cost-competitive with current fuels that are utilized in the aviation industry. However, this requirement is beyond the scope of this research because Mercurius will not have submitted the cost parameters of REACH at the time of this investigation's conclusion. Second, a sufficiently large total land mass would need to exist because large quantities of corn stover would be required to supply a significant portion of the aviation industry's fuel consumption demands. This requirement was addressed in the literature review of this investigation, as a large amount of cornfield infrastructure already is in existence. Third and finally, corn stover would have to successfully be scaled-up through the levels of a biofuel production process, and the in-lab research behind this investigation was conducted in part for this requirement. The LORRE research team tested the REACH process to see if it could successfully be scaled past the laboratory level, and specifically the team conducted the first two stages, acid-hydrolysis and condensation.

5.2 Summary of the Study

The research question posed by the current investigation was: Is corn stover a feasible biomass feedstock source for a sustainable biofuels pathway that utilizes the Renewable Acid-Hydrolysis Condensation Hydrotreating process?

This investigation's literature review researched the economic and ecological factors related to corn stover harvest, compared corn stover to alternative biomass feedstocks (primarily algae) that are used in commercial production of biojet fuel, and studied Mercurius' descriptions of the underlying chemistry behind REACH as well as the process' overview. The methodology of this investigation outlined the experimental setups and measures of success for the in-lab research conducted at the LORRE labs. The methodology also presents the HPLC system's technique and presents examples of the output analysis data.

5.3 Findings of the Study

During the active time of this investigation, the LORRE research team conducted condensation reactions and utilized two set-ups for these trials: the standard water bath and the jacketed vessel reactor. Throughout the duration of a reaction, samples were taken and prepared for a HPLC system. The HPLC system would process the samples against a set of pre-determined standards and subsequently produce an analysis summary, the MSS, for the user. The MSS displayed various forms of data, but the key piece of information that it presented was the volume or amount of each compound in each sample. Thus, the LORRE research team used the MSS's to track the volume of the two main ingredient compounds, 5-MF and LA, throughout condensation reactions. During the reactions, 5-MF and LA reacted together to form new compounds, and so the final volume was less than the original amount. If the volume of 5-MF had been converted more than 50% and or the volume of LA had been converted more than 20%, than a successful reaction had occurred.

During the time the LORRE research team conducted condensation experiments, five reactions were run completely and had full HPLC analyses taken. Out of these five reactions, four of them achieved at least one of the measures of success (either 5-MF's or LA's) and two of the reactions achieved both measures. Additionally, both the standard water bath and jacketed vessel reactors proved to yield successful conversions of either 5-MF or LA. The standard water bath reactor yielded successful results at 75° C, although it was the maximum temperature achievable, with a single catalyst addition and a run-time of 24 hours. The jacketed vessel reactor yielded its most successful results at 120° C with a single catalyst and a run-time of 24 hours.

5.4 Recommendations for Future Investigation into REACH's Scale-Up Potential

At the time of this investigation's conclusion, the LORRE research team was still investigating double-catalyst condensation reactions, which showed potential to meet the measures of success, as well as investigating the use of a new catalyst, potassium hydroxide (KOH).

However, the LORRE research team's in-lab findings show that REACH's second stage, condensation, can indeed yield successful results of converting the chemical components into new, desired compounds. The desired compounds are carbon chains with some oxygen molecules prevalent, and these chains are then processed through a hydrotreating unit. The hydrotreating unit deoxygenates the carbon chain and hydrogenates the system, so that hydrocarbon chains are produced with low levels of oxygen. This type of compound is desired because it mimics the petroleum-based fuel's carbon chains, and it is known as a drop-in fuel intermediate.

The LORRE research team's in-lab findings suggest that REACH can successfully be scaled-up form the small-batch laboratory level. At the time of this investigation's conclusion, collaborations with Dr. Clay Wheeler, CBE – University of Maine, to conduct hydrotreating experiments were still underway, and were yielding successful results. Thus, this investigation makes the recommendation that the REACH process should be scaled-up from the small-batch laboratory level assuming that the hydrotreating experiments will produce the desired hydrocarbon chains devoid of oxygen molecules.

LIST OF REFERENCES

ASTM Compass. (2016*). Standard specification for aviation turbine fuel containing synthesized hydrocarbons: Active standard ASTM D7566.* Retrieved from https://compass.astm.org/EDIT/html_annot.cgi?D7566+16b

Biomass. (n.d.). In *Merriam-Webster online.* Retrieved from http://www.merriam-webster.com/dictionary/biomass

Brown, R.C., & Brown, T.R. (2012). *Why are we producing biofuels? Shifting to the ultimate source of energy.* Ames, IA: Brownia LLC.

Buckmaster, D.R. (2008). Assessing activity access of forage or biomass. *American Society of Agricultural and Biological Engineers, 51*(6), 1879-1884. ISSN 0001-2351

Clarens, A.F., Resurreccion, E.P., White, M.A., & Colosi, L.M. (2010). Environmental life cycle comparison of algae to other bioenergy feedstocks. *Environmental Science Technology, 44*(5), 1813-1819. Doi: 10.1021/es902838n

Clark, Jim. (2007). *High performance liquid chromatography – HPLC*. Retrieved from http://www.chemguide.co.uk/analysis/chromatography/hplc.html

IUPAC Gold Book. (2014, February 24). *Condensation reaction*. Retrieved from http://goldbook.iupac.org/C01238.htm

Doran, T. (2014, April 15). Corn stover-to-ethanol plant nears reality. *AgriNews*. Retrieved from http://agrinews-pubs.com/Content/News/Markets/Article/Corn-stover-to-ethanol-plant-nears-reality-/8/26/10157

Drop-In Jet Fuel Blend. (2016). In *CAAFI online glossary.* Retrieved from http://www.caafi.org/resources/glossary.html#D

Edwards, W. (2014a). *Economics of harvesting and transporting corn stover*. Iowa State University: Extension and Outreach. Retrieved from https://store.extension.iastate.edu/Product/Economics-of-Harvesting-and-Transporting-Corn-Stover

Edwards, W. (2014b). *Estimating a value for corn stover*. Iowa State University: Extension and Outreach. Retrieved from https://www.extension.iastate.edu/agdm/crops/pdf/a1-70.pdf

Federal Aviation Administration. (2005, January). *Aviation and emissions: A primer*. Retrieved from http://www.faa.gov/regulations_policies/policy_guidance/envir_policy/media/aeprimer.pdf

Feedstock. (n.d.). In *Merriam-Webster online.* Retrieved from http://www.merriam-webster.com/dictionary/feedstock

Gustafson, C. (2013). *New energy economics: Corn stover harvest challenges*. North Dakota State University Agriculture Communications. Retrieved from http://www.ag.ndsu.edu/news/columns/biofuels-economics/new-energy-economics-corn-stover-harvest-challenges/ , NDSU Extension Service

Indiana Corn Growers Association. (2016). *About ICGA.* Retrieved from http://www.incorn.org/index.php/icga/about-icga

Indiana Corn Marketing Council. (2016). *About ICMC*. Retrieved from http://www.incorn.org/index.php/icmc/about-icmc

International Air Transport Association. (2012, November). *IATA guidance material for biojet fuel management*. Retrieved from https://www.iata.org/publications/Documents/guidance-biojet-management.pdf

Kilaz, G., Lopp, D.W., & Simmons, R.A. (2014). *Streamlining corn stover pre-processing and reducing feedstock costs for the Mercurius REACH process*. Purdue University, Department of Aviation Technology

Kilaz, G., Lopp, D.W., & Mosier, N. (2015). *Mercurius REACH process scale-up*. Purdue University, School of Aviation and Transportation Technology, AirTIES, and LORRE

Macdonald, J.M. Penni, K., & Hoppe, R.A. (2013). *Farm size and the organization of U.S. crop farming*. United States Department of Agriculture, Economic Research Report 152. Retrieved from http://www.ers.usda.gov/media/1156726/err152.pdf

Mercurius Biorefining Inc. (2016). *Welcome to Mercurius!* Retrieved from http://www.mercuriusbiofuels.com/index.html

Mercurius Biorefining Inc. (n.d.). *REACH technology*. Retrieved from http://www.mercuriusbiofuels.com/Technology.html

Pennington, D. (2013, March 20). *Corn stover: What is its worth?* Michigan State University Extension. Retrieved from http://msue.anr.msu.edu/news/corn_stover_what_is_its_worth

Petter, R., & Tyner, W.E. (2014). Technoeconomic and policy analysis for corn stover biofuels. *ISRN Economics, 2014,* 2-15. doi: 10.1155/2014/515898

Thompson, J., & Tyner, W.E. (2011). *Corn stover for bioenergy production: Cost estimates and farmer supply response*. Department of Agricultural Economics, Purdue University

U. S. Department of Agriculture. (2015, June 30). *Acreage*. Retrieved from http://www.usda.gov/nass/PUBS/TODAYRPT/acrg0615.pdf

U.S. Energy Information Administration. (2016a). *Carbon Dioxide emissions coefficients*.
Retrieved from https://www.eia.gov/environment/emissions/co2_vol_mass.cfm

U.S. Energy Information Administration. (2016b). *Frequently Asked Questions: How much petroleum does the United States import and export?* Retrieved from http://www.eia.gov/tools/faqs/faq.cfm?id=727&t=6

Wuerthner, G. (2002). The truth about land use in the United States. *Watersheds Messenger,* Vol. IX (2). Retrieved from https://www.westernwatersheds.org/watmess/watmess_2002/2002html_summer/article6.htm

Xie, R., Tu, M., Yu, Y., Adhikari, S. (2011). Improvement in HPLC separation of Acetic Acid and Levulinic Acid in the profiling of biomass hydrolysate. *Bioresource Technology,* 102. Retrieved from http://apps.webofknowledge.com/full_record.do?product=UA&search_mode=GeneralSearch&qid=2&SID=1Ef4N5EivkN1WtcEhXo&page=1&doc=8