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Production of Transportation Fuel and Potential Biomass source  
for use in Biorefinery**

Andrew James Murphy

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Selected Topics in the Utilization of Natural Resources:

Production of Transportation Fuel and Potential Biomass source for use in Biorefinery

By

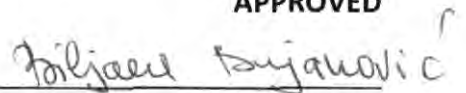
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With Honors

December 2014

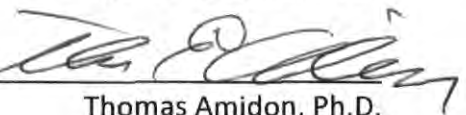
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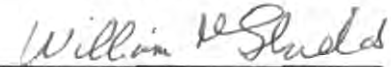
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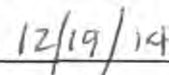
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## Preface

This Report contains research done from two different projects in the spring and summer of 2013. The first section covers research done in the spring at SUNY-ESF, in the lab of Dr. Biljana Bunanovic. I worked under graduate student Chen Gong and research assistant Derek Corbett. My work was on the potential use of wheat straw in a biorefinery. At the conclusion of the semester I presented my work at the 2013 SUNY-ESF Spotlight on Research and also had my poster shown online for The Earth Day Global Poster Session 2013.

The second section covers the work done during my 10 week Research Experience for Undergraduate (REU) at Auburn University over the Summer. I worked under graduate student Shaima Nahreen in the lab of Dr. Ram B. Gupta. My work focused on extracting fermentation products of an adsorbent material that could then be converted into long chain hydrocarbons through a process developed by Shaima Nahreen. At the conclusion of the REU there was a Poster session where I presented my work. I also presented this work at the 2014 SUNY ESF Spotlight on Research

## Acknowledgements

I would like to thank my advisors, Dr. Biljana Bujanovic(ESF) and Dr. Ram B. Gupta (Auburn) for providing guidance and helping me consider the larger implications of my work. I would also like to thank Chen Gong, Derek Corbett and Shaima Nahreen for helping me in the lab with my experiments and making my learning experience a fun one. I would not be the student, learner or person I am now without these incredible experiences and all of the new friends I gained along the way.

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### III. List of Abbreviations

LCB	Lignocellulosic Biomass
EISA	Energy and Independence and Security Act, 2007
DP	Degree of Polymerization
OD	Oven Dry, weight of sample
HWE	Hot Water Extraction
ABE	Acetone-Butanol-Ethanol
CHP	Combined Heat and Power
A/W	Acetone/Water
E/T	Ethanol/Toluene
DCM	Dichloromethane
NIR	Near Infrared
HHV	Higher Heating Value
AOA	Anti-Oxidative Activity
REU	Research Experience for Undergraduates
GHG	Green-House Gas
EISA	Energy Independence Security Act

HHV	Higher Heating Value
DP	Degree of Polymerization
TOC	Total Organic Carbon
HPLC	High Performance Liquid Chromatography

## 0.1 Motivation

The hydrocarbon economy that has formed the backbone of western civilization for the past 100 years has started to diminish, and will become unsustainable in the next couple decades. Furthermore, the necessity to decrease pollution has spurred the development of environmentally-friendly technologies.<sup>1</sup> These reasons have brought about great interest to the possible transition to lignocellulosic-based technologies. The concept is to have nature as a permanently renewing production chain for chemicals, materials, fuels, cosmetics and pharmaceuticals that would be carbon neutral. The National Renewable Energy Laboratory defines biomass as organic matter available on a renewable basis, while lignocellulosics indicate the biomass in which the two major components are lignin and cellulose. Lignocellulosic biomass (LCB) includes forest and mill residues, along with agricultural residues and grasses. LCB is naturally abundant throughout the US, with 1.3 billion dry tons that could be sustainably harvested.<sup>2</sup> The use of biomass would also improve the United States' national security by being able to produce liquid fuels from biomass derivatives, reducing the dependence on foreign countries. It would also considerably improve the balance of trade for the USA. With these considerations in mind, Congress passed the Energy Independence and Security Act of 2007, referred to as EISA. This set the goal for the United States to produce 36 billion gallons of biofuel by 2022, with 21 billion gallons coming from non-corn biomass sources. There are currently 200 ethanol plants, producing 13 billion gallons of ethanol per year<sup>3</sup>, with a 36 billion dollar impact, creating 35,000 jobs. If the current goal for 2022 holds, this sector is projected to grow to a 368 billion dollar industry with 2.4 million jobs<sup>3</sup>, creating sustainable, American jobs. The location of biomass in rural areas would benefit these areas with new industry.



## 0.2 Biorefinery

The industry recommended to support EISA's goals would be biorefineries. A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, heat, and high-value chemicals. The power of a biorefinery is supported by economies of scale and by efficient use of all incoming resources. In a petroleum refinery, 5% of the raw material is converted to chemical products, while the rest goes to fuel and energy, very similar to a biorefinery. The use of carbohydrates as a chemical raw material will eliminate the need for several capital intensive, oxidative processes used in the petroleum industry. Biomass carbohydrates provide a viable route to products such as alcohols, carboxylic acids, and esters. Natural products are also stereo- and regio-chemically pure, able to reduce dependence on expensive chiral catalysts and complex synthesis that are currently required to selectively introduce chemical functionalities into petrochemicals.<sup>1</sup>

One example of the biorefinery used as an alternative to the petroleum refinery is the production of poly lactic acid from fermentation versus chemical synthesis from acetaldehyde and hydrogen cyanide. At present the two are very cost competitive. However, with fermentation improvements and use of cheap agricultural residues the costs will be significantly reduced. One major problem with this and other fermentation products, like with the production of 1,3 propanediol (fibers), is the separation and purification step which accounts for 40-80% of costs.<sup>4</sup> This will be further *discussed in the second section of research performed at Auburn University.*

*Currently there are industries that are good examples of well-developed biomass conversion infrastructure: pulp/paper mills and corn ethanol facilities.<sup>1</sup> Along with pulp used for paper, Kraft pulp mills produce tall oil and turpentine which add profitability. Annual production of tall oil and turpentine, which have been shown to be useful in biodiesel applications, is in the range of 700 million liters<sup>5</sup>. Ethanol is looked at as a very promising fuel to replace gasoline as it can be produced at a relatively*

modest cost, and would significantly reduce greenhouse gases, up to 86%<sup>5</sup>. With a pre-extraction step in a Kraft pulp mill, 14 million tonnes of hemicelluloses could be extracted and used to make bioethanol, while also enhancing pulping.<sup>5</sup> With a pulp mill having ~50% of the technology that would be necessary to contribute to biofuels, it could be promising to add infrastructure. Pre-extraction of hemicelluloses would have to be optimized in accord with the strength of paper produced. However, pre-extraction would help debottleneck recovery boiler-limited mills as isosaccharinic acids (degraded hemicelluloses) only produce 25% of the heat while taking up a much larger proportion of the volume.<sup>5</sup> Pre-extracting hemicelluloses has many beneficial effects, including improved impregnation of white liquor, improving pulp properties, while reducing pulping times.<sup>5</sup> In addition, bark that is currently burned has been shown to have high amounts of extractives that could add value prior to combustion.<sup>5</sup>

One major advantage of starch based biomass (e.g. cereal grains) is that the sugars are more easily broken down because of their much more accessible glycosidic bonds, due to lack of hydrogen bonding and a crystalline structure. This made them the initial source of biomass used to make fuel and chemicals; however, starch based biomass does tend to have some drawbacks. Lignocellulosic biomass, especially from trees, can be harvested year round and does not deplete the nutrients in the soil, like corn. Another major problem with corn and other starch based biomass (e.g. cereal grains) is that with the growing demand for food, using starch to produce ethanol becomes socially and economically undesirable.

### 0.3 Chemical Structure

Lignocellulosic biomass is comprised of three major components: cellulose, hemicelluloses, and lignin. Cellulose is a homopolysaccharide characterized by the presence of  $\beta$ -D-glucopyranose units, connected by  $\beta(1\rightarrow4)$  glycosidic bonds forming a linear chain. Two glucopyranose units make cellobiose

(fig. 1), the repeating unit. Cellulose in LCB has a degree of polymerization of around 5000 for hardwoods<sup>7</sup>. These linear chains form two regions of cellulose: crystalline and amorphous. Amorphous regions of cellulose lack a higher degree of hydrogen bonding and can be easily broken down in glucopyranose monomers for fermentation. However, the crystalline regions of cellulose which make up 50-70%<sup>7</sup> of the cellulose found in biomass is very difficult to penetrate and break down due to large amounts of hydrogen bonding, making this a major area of research to make lignocellulosic biorefineries viable.

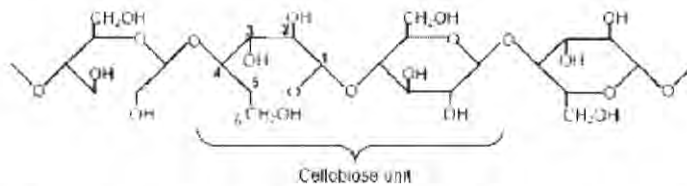


Figure 1. Structure of cellulose, with cellobiose repeating unit<sup>6</sup>

Hemicelluloses are complex, branched heteropolysaccharides containing glucose and a few other sugars that make up the majority of hemicelluloses, depending on type of biomass (hardwood vs softwood vs monocotyledons). Two are hexoses (6-membered sugars): mannose and galactose. The two other are pentoses (5-membered sugars): xylose and arabinose. Xylans make up the majority of the hemicelluloses in hardwoods and monocotyledons, making up 25-35% of the raw weight of LCBs. Xylans are the second most abundant polysaccharide on the earth behind cellulose. As shown in figure 2, xylans are formed by β-(1→4) attached-D-xylopyranoside units. This backbone can be substituted with O-acetyl groups at the O-2 or O-3 position of D-xylopyranoside units, as shown in figure 2. It can be further substituted with units of L-arabinofuranose or D-glucuronic acid (fig. 5), which can then be further acetylated or methylated at the C-4 position (fig.5).

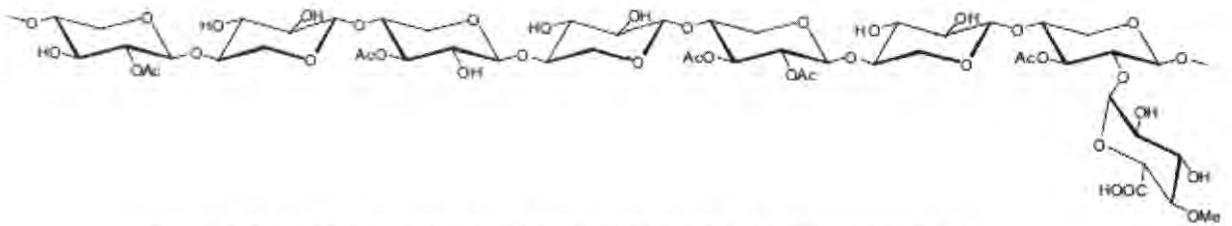


Figure 2. Representative structural formula for hardwood glucuronoxylan<sup>9</sup>

For softwoods the hemicellulose content is much more diverse and contains three major

different constituents. The first makes up 10-15% of the LCB oven dry (OD) weight<sup>9</sup>, and is comprised of  $\beta$ -(1 $\rightarrow$ 4) linked backbone of gluco- and manno- pyranose units, which can also be acetylated at the O-2 and O-3 positions, although not as frequent as in hardwoods.<sup>9</sup> Another 5-8% of the OD weight of softwoods is made up of the same glucomannan backbone; however it is substituted with galactopyranose attached by  $\alpha$ -(1 $\rightarrow$ 6) linkages (fig. 3).

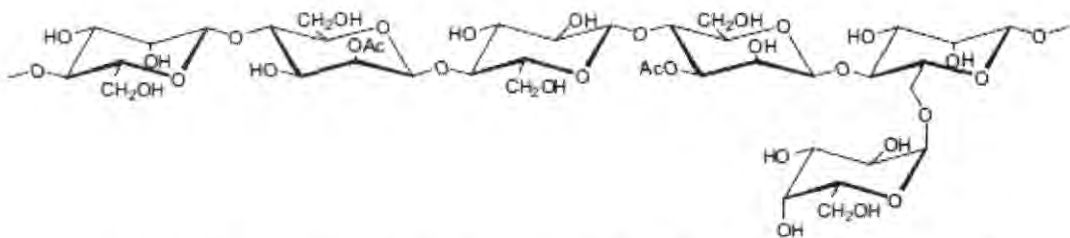


Figure 3. Representative structural formula for softwood galactoglucomannan<sup>9</sup>

The last major hemicellulose constituent makes up 7-10% of the OD mass of softwoods<sup>9</sup>. It has a xylan backbone and is substituted by arabinofuranose and methylglucuronic acid, as shown in figure 4.

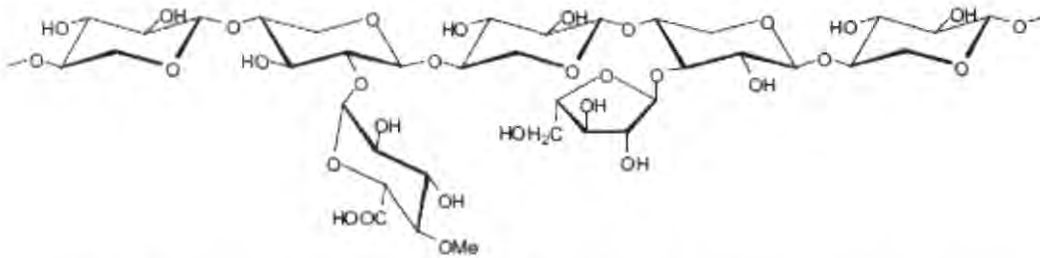


Figure 4. Representative structural formula for softwood arabino-4-O-methylglucuronoxylan<sup>9</sup>

Figure 5 (below) shows the differences in xylans in hardwoods, softwoods, and monocotyledons, such as wheat straw and corn cobs. As shown the grasses/cereals are much more substituted. This will be further discussed in the lignin section.

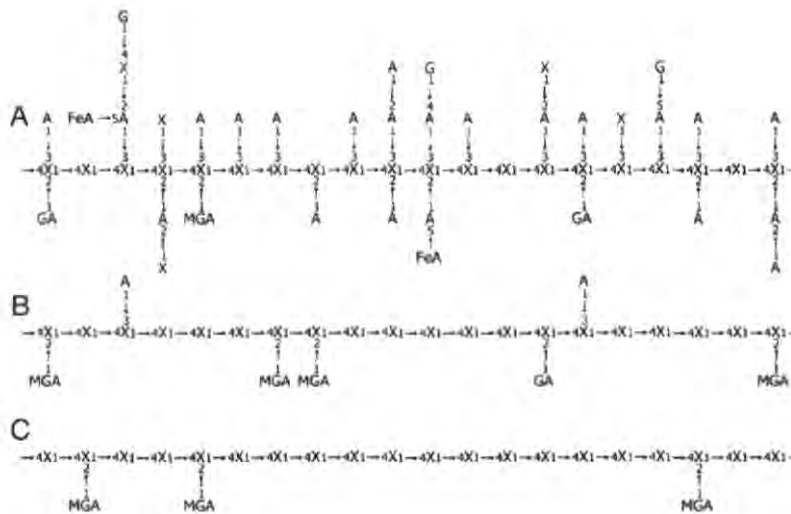


Figure 5. Representative chemical structure of xylans: A) grasses and cereals, B) Softwood, and C) hardwood, that reflect the major linkages and side-chains with their approximate frequencies. (X-xylose, A-arabinose, G-galactose, GA-glucuronic acid, MGA-4-O-methyl-glucuronic acid, FeA- ferulic acid)<sup>8</sup>

The degree of polymerization, DP of xylans is 100-200. Xylans may be broken down to make xylitol (sweetener) and/or bioethanol. The attached acetyl groups in hardwoods and monocotyledons are very beneficial in a Hot Water Extraction, which will be discussed later. Hemicelluloses are much

more easily degraded and removed, due to a lack of crystalline structure and a much smaller DP, in comparison to cellulose.

Lignin is the last major constituent of lignocellulosic biomass. Characterization of the composition and structure of lignin will help maximize the exploitation of LCBs as a feedstock in a biorefinery. Lignin is an amorphous, highly-polymerized aromatic substance which forms the middle lamella and cements the fibers together and is crucial for structural integrity of the cell wall. The chemistry of lignin is complex, but can be described as a polymerization product of three hydroxycinnamyl alcohol monomers-monolignols: *p*-coumaryl(4-hydroxycinnamyl), coniferyl(4-hydroxy-3-methoxycinnamyl) and sinapyl(3,5-dimethoxy-4-hydroxycinnamyl), shown in figure 6. All three of these alcohols are polymerized by enzymatically generated radicals. These monolignols produce respectively *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) phenylpropanoid lignin units when incorporated into the lignin polymer.<sup>10</sup> H, G, and S units of lignin are commonly bonded by ether and C-C bonds, of which the most abundant is the  $\beta$ -O-4 ( $\beta$ -aryl ether) linkage. Lignin in hardwoods and monocotyledons contains S and G constituents, with monocotyledons containing somewhat more H-units than hardwoods. Softwoods contain mainly G and trace amounts of H units.<sup>10</sup> In grasses, *p*-hydroxycinnamates (*p*-coumarates and ferulates) occur. *p*-Coumaric acid acylates the  $\gamma$ -OH of the lignin side chain, whereas ferulic acid acylates the cell wall polysaccharides and participates in both polysaccharide-polysaccharide and lignin-polysaccharide cross coupling reaction; becoming integrally bound into the lignin polymer.<sup>10</sup> A structural characterization of wheat straw lignin shows a H:G:S ratio of 6:64:30.<sup>10</sup>



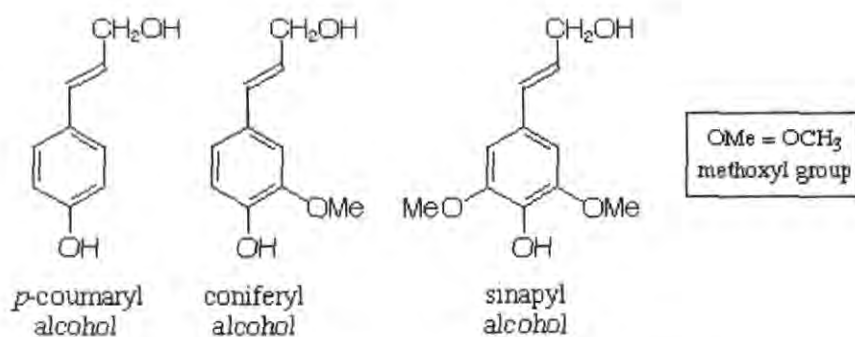


Figure 6. Cinnamyl alcohol precursors of lignin<sup>11</sup>

For the production of high quality paper lignin needs to be extracted from the pulp, in a process which is both expensive and environmentally hazardous, requiring large amounts of energy and chemicals. Lignin is a barrier in accessing cellulose to produce ethanol, making a pretreatment step necessary. Lignin can be chemically modified and made into high value aromatic products. These include antioxidants, adhesives, carbon fiber, and vanillin,<sup>12</sup> all of which could potentially be important for the economic feasibility of a biorefinery.

#### 0.4 Pretreatment

There are a number of issues that need to be addressed in order to make the lignocellulosic-based technology viable. Treating raw lignocellulosic biomass with acid or enzyme leads to a minimal amount of glucose, due to lack of accessibility and inhibition by lignin and degradation products of hemicelluloses, making it uneconomical. An effective pretreatment step must remove hemicelluloses and their attached acetyl groups, remove or alter lignin, increase pore volume and internal surface area, reduce the DP of cellulose, and decrystallize cellulose (fig. 7). Some of the criteria that qualify pretreatment as appropriate include requiring minimal chemical and energy input, being suitable for diverse biomass sources and limiting the formation of inhibitors. The production of fuels and chemicals

from LCB requires one or multiple pretreatment steps, increasing the cost of production. For LCB, different pretreatments are being tested for effectiveness and energy use, but a cost effective pretreatment process remains one of the largest hurdles to be overcome to produce chemicals and fuel from biomass effectively.

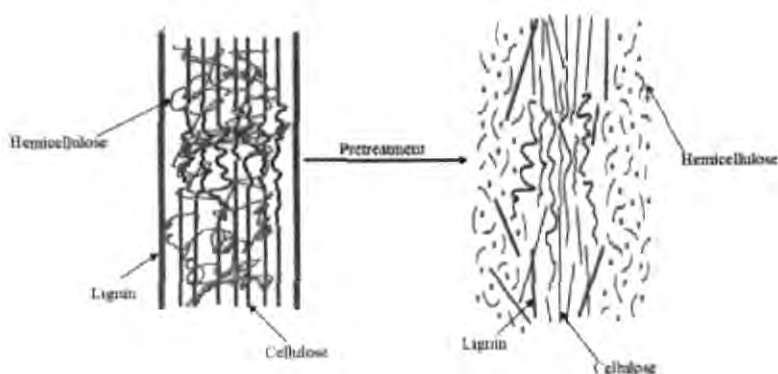


Fig. 7 Effect of pretreatment on lignocellulosic biomass<sup>6</sup>

During the past five to ten years, a large number of pretreatment methods have been developed, including alkali treatment, ammonia explosion and others that have been able to produce a higher than 90% sugar yield.<sup>6</sup>

The Biorefinery proposed at SUNY ESF is based on the first, environmentally friendly, step of hot-water extraction (HWE) as a pretreatment which removes easily accessible hemicelluloses, inorganics soluble in water, hydrophilic extractives, and some easily removable lignin. Most of the studies of HWE have been performed on different hardwoods resulting in the dissolution of most of the xylans (model species: sugar maple, *Acer saccharum*, abundant species in Northeast US). Since it only uses water and the lignocellulosic biomass, the extraction itself is environmentally acceptable because it requires no acidic, caustic, or hazardous chemicals. This leaves the hemicelluloses and cellulose relatively undegraded so they can still be effectively converted to chemicals and energy. The hydronium



ions from the water and other compounds generated during the extraction (acetic, uronic, phenolic acids) help catalyze depolymerization of the hemicelluloses.<sup>13</sup> In HWE a small amount of soluble lignin is removed, which is important to indirectly test for percent dissolution of hemicelluloses.

In integrated biorefinery/pulp and paper mills, the optimization of fiber and sugar properties should be performed so each can be used for the most economic benefit. Some ideas are being implemented into the paper industry, where hemicelluloses could be extracted before pulping, to produce ethanol, adding value prior to pulping. Low yield chemical pulps have the greatest potential for value prior to pulping.<sup>1</sup> In Kraft pulping, alkali is used to break down and solubilize lignin. The alkali also solubilizes a large amount of the hemicelluloses as well, making the liquor less effective in removing lignin. If a HWE step was utilized before Kraft pulping it could lead to a larger removal of lignin and shorter cooking times, increasing output from digester. This would also affect bleaching sequences, since lignin remaining is easier to remove, so mills could be more focused on removing chromophoric groups or decreasing the amount of energy that needs to be put in in order to produce a similar product. For bleaching, the removal of hemicelluloses is beneficial since they can contribute to the chromophors in fiber with units such as uronic and hexuronic acids, which are resistant to alkaline pulping and bleaching.<sup>13</sup> The acidic conditions produced in HWE remove acetyl groups and heavy metal ions, which also improves subsequent pulping and bleaching efficiency.

## 0.5 Research Areas

One major topic in biorefining is the source of lignocellulosic material. Wheat straw, the focus of this research at SUNY ESF, is widely abundant around the world and is usually burned instead of being collected. In 2011, 900 million tonnes of wheat straw was produced worldwide.<sup>10</sup> One focus of this work was to characterize the chemical composition of wheat straw to determine how much cellulose and

hemicelluloses could be available (hydrolyzed) to make fuels and chemicals. Another important goal was to assess the amount of lignin removal *via* HWE to better estimate its utility for producing high-value products. Hot-Water Extraction was also performed to estimate its benefits on the higher heating value and alteration in chemical composition.

Another major topic of biorefining involves the types of fuels that should be produced. Ethanol has been produced in large amounts through fermentation. Other fuels have been proposed as well; one example butanol, which has many desirable properties, has been researched through Acetone-Butanol-Ethanol (ABE) fermentation. The work at Auburn University focused on purifying and separating all three solvents produced from ABE fermentation, with a novel catalytic process to create long chain hydrocarbons with comparable energy content to jet fuel.

**Part One**  
**Potential Use of Wheat Straw in Biorefinery Based**  
**on Hot-Water Extraction**

## 1.1 Abstract

As the price of corn-based ethanol products is estimated to continue increasing in the near future, lignocellulosics remains the only viable candidate as a renewable source of ethanol production. Wheat straw is grown in over 115 nations under a wide range of conditions, with 300 million tons being produced every year in North America and Europe alone. The Biorefinery proposed at SUNY ESF is based on the first, environmentally acceptable step of hot-water extraction (HWE) as a pretreatment, which removes easily accessible hemicelluloses. Most of the studies of HWE have been performed on different hardwoods (model species: sugar maple, *Acer saccharum*), and confirmed the dissolution of the majority of xylans. This study looked into the use of wheat straw in the HWE-based biorefinery. The chemical composition of wheat straw before HWE was determined by following several TAPPI and other methods used to analyze chemical composition. The HWE was performed in standard conditions proposed for hardwoods (2 hours, 160°C). The effect of HWE on the calorific value of the wheat straw was evaluated and confirmed that the loss of hemicelluloses during HWE results in an increase of energy of combustion of the extracted wheat straw which is a beneficial feature for potential use of hot-water extracted wheat straw as pellets for CHP (Combined Heat & Power) use. In addition, the delignification and deashing effects of HWE were evaluated.

## 1.2 Introduction

Fossil deposits are limited and not renewable on a human civilization time-scale. Along with this there is still a growing demand for food, making use of sugar from starch unfeasible as a fuel compared to lignocellulosic material. In particular, lignocellulosic waste materials, such as agricultural residues represent a large source of renewable biomass. This group includes rice straw, corn stover, and wheat

straw. Wheat straw (*Triticum spp.*) is the most prominent of these agricultural residues. It is the world's most widely grown crop, being grown in over 115 countries in a wide range of conditions. It has been predicted that about 850 Tg ( $8.5 \times 10^{11}$  Kg or  $3.9 \times 10^8$  tons) of wheat residues are produced annually, with about 300 million tons of that being produced in Europe and North America.<sup>13</sup> Different pretreatments of wheat straw represent a major step in the process and have been studied for many years and more intensely in recent years. Pretreatments for biorefinery vary and are similar to those used for woody biomass. The effects of sulfite pretreatment on the component separation and saccharification of wheat straw have been studied recently,<sup>14</sup> along with much research into steam explosion pretreatment.<sup>15,16</sup>

Many of the tests used to determine the chemical composition and the effect of the HWE have only been used on wood species; determining whether these tests are appropriate for use in studying agricultural residues was important for further research into their use in a biorefinery. Wheat straw along with most other agricultural residues is a type of monocotyledons, which typically have a more open structure than wood (lower density and higher porosity). This would lead to the assumption that some standard tests made for wood samples are applicable for agricultural residues. Initially TAPPI methods 412 and 211 were performed to determine the moisture content and ash percentage of the wheat, respectively.<sup>15,16</sup>

The amount of extractives in a sample is very important for use in biorefineries. Several high value products can be made from extractives such, as anti-oxidants. Extractives are low molecular weight organic compounds present in LCB, soluble in neutral organic solvents. The result of the test used to determine the amount of extractives in wood is dependent on how the sample was dried since the wood meal may become less accessible to the organic solvents or some volatile extractives may be lost during drying. Since no single organic solvent is capable of efficiently removing all present extractive,

solvents are usually used in sequence to extract the maximum amount of material. According to TAPPI 204, ethanol-benzene mixture appears to give a more complete removal of solvent extractable substances.<sup>17</sup> Two different solubility tests were run to see their effect on wheat straw. One of the solubility tests was using 1% NaOH, following TAPPI Standard 212, to extract low-molecular-weight carbohydrates consisting mainly of degraded hemicelluloses.<sup>18</sup> This test is commonly used in pulp mills to test for degree of degradation due to heat, light, or fungal decay. Another solubility test that was run was using room temperature water (Cold Water) following TAPPI Standard 207.<sup>19</sup> This method removes *some of the inorganic compounds, tannins, gums, sugars and coloring matter present in wood.*

TAPPI Standard 684 was used to determine the heating value of the wheat straw before and after the HWE.<sup>20</sup> Heating value is important in determining how much heat or power could be provided and in determining if there is any inefficiency in the CHP system. The Klason lignin can be found using TAPPI Standard 222<sup>21</sup> while the acid-soluble lignin is found using UM 250.<sup>22</sup>

Near Infrared spectroscopy (NIR) is similar to IR and measures the vibrational spectroscopy of *bonds in a compound. The near infrared spectrum consists of a combination and overtone bands, rather than the fundamental bands seen in the IR.* Because of this, algorithms are used to analyze subtle differences in spectra and correlate them to differences in the input values from a calibration set, meaning a known set of values is required to use NIR.<sup>23</sup>

### 1.3 Methods

Before analysis, the wheat straw (obtained at CNY Green Market, Syracuse, NY, Fall 2012) was ground to a 40-mesh using a Wiley mill in order to increase the surface area to ensure more complete

reactions during the experiments. The ground sample was then kept in a sealed container to ensure a constant moisture content of the raw sample.

Table I. Methods used for Characterization of Wheat Straw

TAPPI 412 "Moisture in pulp, paper, paperboard and combined board"	Moisture Content
TAPPI 211 "Ash in wood, pulp, paper and paperboard: combustion at 525°C"	Ash content
TAPPI 204 "Solvent extractives of wood and pulp"	Extractives %
TAPPI 207 "Water solubility of wood and pulp"	Cold Water Solubility
TAPPI 212 "One percent sodium hydroxide solubility of wood and pulp"	%1 Sodium Hydroxide solubility
TAPPI 222 "Acid-insoluble lignin in wood and pulp"	Klason Lignin
UM 250 (4% sulfuric acid) "Acid-Soluble Lignin in wood and pulp"	Acid-Soluble Lignin
Kurschner-Hoffer method <sup>23</sup> "New quantitative cellulose determination"	Cellulose %
TAPPI 684 "Gross heating value of black liquor"	Higher Heating Value

Hot Water Extraction was done in duplicates with five gram samples. The sample was extracted at 160°C for 2 hours. The sample was then filtered, allowed to air dry and measured. The moisture content was then performed to calculate the percent of mass lost during the extraction. For the HWE wheat straw samples, a few tests were used to help compare to the original sample. The same modified Klason/Acid-soluble lignin was performed on the extracted wheat straw. The heating value before and after HWE was determined using a bomb calorimetry following TAPPI 684. A modified solvent extraction was performed for the HWE wheat straw in order to remove the extractives that could invalidate the acid-soluble lignin test (polyphenolic extractives). This extraction was done with dichloromethane since



after the HWE a lot of the lignin is 'loosened' up and could be removed if the same solvents were used as before.<sup>25</sup>

The Bruker MPA FT-NIR located in Jahn Lab was used with a willow model to test the amount of cellulose, hemicelluloses and lignin in the wheat straw sample.

All results of determination of chemical composition of wheat straw are expressed in percent based on oven dry (OD) wheat straw.

#### 1.4 Results

Table II. Chemical Composition of Wheat Straw, Compared to NIR and Literature Values<sup>26-9</sup>

	% OD Wheat Straw				
	Cellulose	Lignin	Extractives	Ash	Hemicelluloses (difference)
Sample before HWE	45.20	17.50	3.70	3.70	29.88
Sample after HWE	63.70	17.70	3.00	2.60	13.00
Literature	36.7-38.8	16.6-20.1	----	7.9-9.7	18.0-23.50
NIR	41.69	23.98	----	3.24	31.11

Table III. Effect of Hot Water Extraction on Heating Value

Energy of Combustion Comparison (BTU/lbm)		
Before HWE	After HWE	Improvement
7960.5	8191.3	230.9

Table IV. Effect of Hot Water Extraction on Chemical Composition

HWE yield % OD wheat straw	Lignin dissolved % of original lignin	Ash dissolved % of original ash	Hemicellulose dissolved % of original hemicelluloses calculated value
71	28.10	50	74



Table V. Miscellaneous Wheat Straw Test Values, before HWE

	% OD wheat straw	
Moisture Content	Cold Water Solubility	1% NaOH Solubility
6.86	10.30	40.44

## 1.5 Discussion

The chemical composition of the untreated wheat straw was comparable to several different studies done on wheat straw and the Near Infrared Spectroscopy (NIR). The value that usually interests researchers is the cellulose content because of its use in fermentation to create ethanol. The sample that was tested in the lab showed to have been on the high range of cellulose content when compared to literature cited in Table II. The high solubility of wheat straw in HWE is due to the high amount of hemicelluloses. This is further proven by the 1% NaOH result (40.44%), which is a large value which according to TAPPI means that there is a relatively high level of degraded/damaged hemicelluloses.

For NIR, the willow model used to characterize the wheat straw was disproven when it showed little change in the chemical make-up of wheat straw after HWE and other tests (e.g. 1% NaOH and cold water). For a more accurate determination using the NIR a wheat straw model would need to be developed.

The ash content is quite dependent on the sample and how long it was held in the field after being harvested since a lot of the inorganics could have been washed out (e.g. rain). The lignin content

*found in this study was lower than the average. The moisture content shows that the sample had been at room conditions for an extended duration.*

Table 2 shows that HWE extraction improves the heating value of wheat straw. This agrees with the hypothesis that hemicelluloses decrease the heating value because of their high oxygen content compared to cellulose or lignin. Table 3 shows that a significant amount (28.1%) of lignin was also removed during HWE. If this lignin, because of its high heating value<sup>30</sup>, could be easily incorporated back into the HWE wheat straw it would be very beneficial for making pellets to be used in CHP systems, as well as the production of adhesives or conversion to vanillin.

The solubility tests in Table IV shows a large difference between room temperature water and warm water with a small amount of alkali (1% NaOH). The alkali can solubilize the hemicelluloses along with other low weight compounds in the wheat straw while the cold water only dissolves low-molecular weight compounds, such as inorganics, tannins, and simple sugars. The hemicellulose content of the sample from Table I is almost the same as the difference between the two solubility tests. This shows that even a small amount of alkali is very effective in removing hemicelluloses.

## 1.6 Conclusion

The experiments performed in this study showed that the wheat straw sample had similar chemical composition to that reported in several scholarly articles. The NIR gave quite similar results for the raw sample when using a willow model, although was proven to be inaccurate when it was given different treated wheat straw samples. The HWE yield and delignification was similar to corn cobs, while the delignification was double to what was found for sugar maple. The heating value comparison before

and after HWE should that it increased even with significant delignification, leading to the point that if the lignin could be recovered and put back into the wheat straw effectively then the corresponding pellets would be very useful in CHP.

There are quite a few future studies that could be done to gain a more complete understanding of wheat straw and how it is affected by a HWE. More experimentation on the HWE wheat straw to gain a more comprehensive chemical composition could be done to gain a better understanding of how the HWE affects the chemical composition of wheat straw. Another study that could be done is a determination of how much hemicelluloses and lignin are recoverable from the HWE filtrate. The lignin could be used to make high value products, such as adhesives, along with being added back into the wheat straw to make pellets. The hemicelluloses could be used to make high volume products such as ethanol. One test that can be done is the anti-oxidative activity (AOA) of the extractives obtained from the Ethanol/Toluene and Acetone/Water extractions, along with filtrate from the HWE. This would show the potential of production of anti-oxidants from a biorefinery.

## **Part Two**

**Biofuel Production: Separation & Purification of Fermentation Products**

**from *Clostridium* for Transportation Fuels**

## 2.1 Abstract

The US has set the goal to produce 36 billion gallons of biofuel by the year 2022. ABE fermentation produces a series of solvents (Acetone, Butanol, Ethanol) that can be purified or upgraded to drop-in transportation fuels. Despite significant advances in ABE fermentation, inefficient product removal and purification from the dilute fermentation broth delay commercialization of this process. Advances in ABE fermentation will be examined, along with an investigation into the new techniques of product separation and purification. From the literature, adsorption is one of the most energy and cost effective methods to increase the concentration of ABE with activated charcoal showing good selectivity towards ABE products. Advances in adsorption-desorption techniques will be discussed along with production of 'green' hydrocarbons.

## 2.2 Introduction/ Overview

The importance of developing technologies to produce biofuels in the near and far future in the US will be discussed. Roadblocks in this process will be discussed, along with new advances that hope to significantly reduce this problem. A literature review which will be presented is focused on butanol separation and on the production of biofuels as a whole. The aim of this paper is to discuss the purification/separation process that was developed during my Research Experience for Undergraduates (REU) in the Summer of 2013, as well as to discuss its importance in producing 'green hydrocarbons' and look into its implication for the future.

With the need for the United States to reduce dependence on foreign fossil fuels, Congress passed the Energy Independence and Security Act of 2007, referred to as EISA<sup>3</sup>. This set the goal for the United States to produce 36 billion gallons of biofuel by 2022, with 21 billion gallons coming from non-corn

biomass sources. There are currently 200 ethanol plants, producing 13 billion gallons of ethanol per year<sup>3</sup>, with a 36 billion dollar impact, creating 35,000 jobs. If the current goal for 2022 holds, this sector is projected to grow to a 368 billion dollar industry with 2.4 million jobs, creating sustainable, American jobs<sup>3</sup>. These processes could then be replicated in many other countries, most of which do not have the financial capabilities of the US.

Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) has been used widely as a fuel source because it can be used in a 10% blend with gasoline with no engine modifications needed and can be produced cheaply because no pretreatment is required<sup>31</sup>. Ethanol, compared to gasoline, has a higher octane number, broader flammability limits, higher flame speeds, and higher heating value (HHV). This all leads to higher compression rates and a shorter, leaner, more efficient burn, reducing  $\text{NO}_x$  emissions<sup>31</sup>. However, further implementation is a problem as ethanol has a high aqueous solubility, is hygroscopic and is corrosive. Butanol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ) being more energy dense than ethanol, and having none of the same demeaning qualities, presents great potential as a transportation fuel<sup>31</sup>.

ABE fermentation, also known as solvent fermentation, produces a series of solvents, which are acetone ( $\text{CH}_3\text{COCH}_3$ ), n-butanol (referred to hereafter as butanol) and ethanol. These solvents are normally produced in a 3:6:1 ratio with a product concentration of 20-25 g/L<sup>32</sup>. This fermentation process is carried out by a *Clostridium* microbial strain, usually *Clostridium acetobutylicum* or *beijerinckii*.

Since 1950, butanol production has been done petrochemically through either the oxo or aldo processes<sup>32</sup>. Before 1950, ABE produced by fermentation was second only to fermentation ethanol in volume of production<sup>3</sup>. Fermentation substrate costs made this process uncompetitive with petrochemical processes based on the relatively low oil prices of the 1950s<sup>32</sup>. Another exciting breakthrough is that the fermentation products from ABE have been converted into long chain hydrocarbons with an energy content similar to that of jet fuel, producing 'green hydrocarbons' that can

be as a drop-in fuel with the existing petroleum dedicated infrastructure<sup>31</sup>. However, research and work remains to be done to make the overall process from biomass to butanol and/or green hydrocarbons competitive with the petroleum industry. Rising oil prices have increased the urgency of addressing the work remaining to be done.

### 2.3 Understanding the Problem

For lignocellulosic biomass, different pretreatments are being tested for effectiveness and energy use, but a cost effective pretreatment process remains one of the largest hurdles to be overcome to produce chemicals from biomass effectively<sup>30</sup>. Lignin is the major roadblock in utilizing biomass. Lignin covers the cellulose and hemicelluloses and binds with the enzyme that breaks down cellulose, resulting in less of the enzyme being available for hydrolysis. An effective pretreatment step must remove hemicelluloses and their attached acetyl groups, remove or alter lignin, increase pore volume and internal surface area, reduce the degree of polymerization (DP) of cellulose, and decrystallize cellulose<sup>30</sup>. Some of the criteria that an ideal pretreatment will satisfy are minimal chemical and energy input, suitability for diverse biomass sources, and limited or no formation of inhibitors. By and large, if the long chain polysaccharides are not broken down economically into sugars for the fermentation then the EISA goal that the U.S. set will not come to fruition.



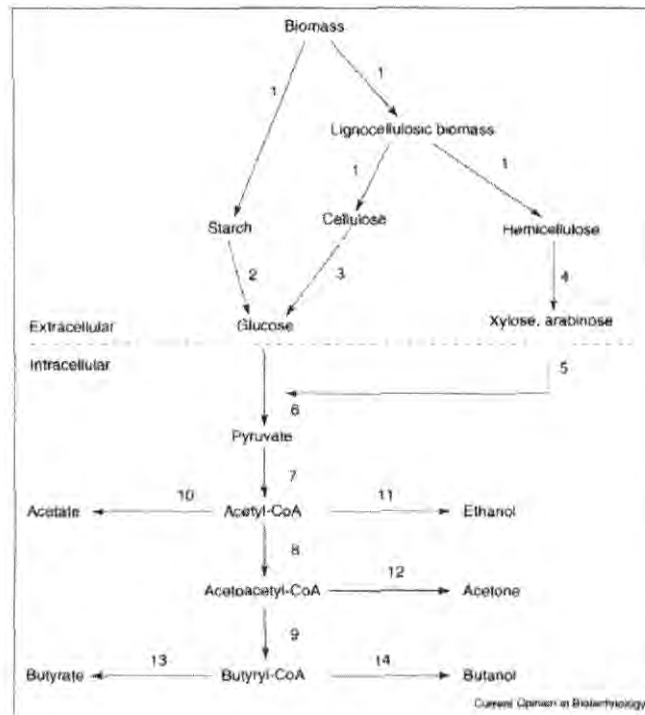


Figure 1. Mechanism of ABE production by *Clostridium acetobutylicum*<sup>32</sup>, showing the process of taking biomass and making it into acetone, butanol and ethanol.

Many obstacles have been overcome during fermentation to improve butanol yield. How *Clostridium* produces these solvents is shown in fig. 1. One major problem in the fermentation is that the cell walls become increasingly permeable as butanol concentration increases, leading to a higher sugar uptake which kills the bacteria<sup>33</sup>. Researchers are looking for ways to solve this problem, either through making *Clostridium* more resistant to butanol or a method to remove butanol or the bacteria effectively from the fermentation. Cells can be immobilized using adsorption so they can be easily removed from the fermentation broth. Adsorption is extremely beneficial for several reasons. It is a simple technique that requires no chemicals, works in anaerobic conditions and helps form a biofilm which reduces diffusion resistance<sup>33</sup>. Genetics have also played a major role in increasing solvent production by over 30%<sup>34</sup>. It has been identified recently that regulating NADP via methyl viologen can increase butanol production while decreasing acetone production<sup>35</sup>. This is significant since acetone in the deoxygenation process yields mainly gaseous products (C<sub>2</sub>-C<sub>6</sub>) that cannot be used for transportation fuels. Future



advances in this area will help in the separation and purification of the fermentation products and improve the overall process feasibility.

After the separation and purification step the butanol can be sold as a platform chemical or blended for transportation fuel. One novel technique that has gained attention lately is the production of 'green hydrocarbons' through a catalytic deoxygenation/ dehydration process<sup>31</sup>. In this process a model mixture of acetone, butanol and ethanol (3:6:1) is pumped through a packed bed of catalyst (alumina/zeolite) in a continuous process at relatively high temperature and pressure (400-600°C, 3-13 bar). This process produces three phases: a gaseous phase, an aqueous phase and an organic phase. The organic phase contains hydrocarbons (C<sub>5</sub>-C<sub>16</sub>) that have comparable energy content to that of jet fuel (~40 KJ/g). The dehydration/deoxygenation step involves cross reactivity of the fermentation products, giving myriad compounds<sup>31</sup>. This process is still at the lab scale and much work needs to be done to make it viable, such as using actual fermentation broth from a separation/purification process and determining the effects of butyric acid. In order for this process to be scaled up, the reactants (acetone, butanol, ethanol) need to be purified economically so little to no water and other by-products are present.

Because of butanol toxicity, many different methods have been developed to continuously remove butanol *in situ*, along with the other major products. This can be done by membrane separation or immobilizing the cells in order to easily separate the bacteria from the broth<sup>31,32</sup>. Major problems arise when trying to purify the fermentation broth that contains the solvents produced by ABE fermentation. The first problem is that the products are in very low concentration (~25g/L), which is a quarter to an eighth of what is produced in ethanol fermentation<sup>36</sup>. The other significant problem is the major product butanol has a higher boiling point (118°C) than water (100°C). This means that the

distillation process used commonly for ethanol production is not economically feasible for purifying the ABE fermentation products, mainly butanol.

There are a number of other separation/purification techniques that can be used and have been researched to determine their effectiveness. These techniques include: gas stripping, liquid-liquid extraction, perstraction, pervaporation and adsorption.

Gas stripping has an advantage because it can be done *in situ*, where H<sub>2</sub> and CO<sub>2</sub> gas produced by the fermentation can be bubbled up through the fermentation broth, capturing ABE products. From here the gas can be run through a condenser to recover the product and then be recycled back through the system. This makes this process very simple and economical<sup>32</sup>.

In liquid-liquid extraction, a water-insoluble organic solvent, commonly oleyl alcohol (CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>-CH=CH-(CH<sub>2</sub>)<sub>8</sub>OH), is mixed with the fermentation broth. Butanol is more soluble in the organic phase than the broth, causing the butanol to become concentrated in the solvent. The organic and aqueous layers are easily separated, while the nutrients, water and proteins are not removed. However several concerns are brought about when using liquid-liquid extraction. These include toxicity to the cells, formation of emulsions, loss of the extraction solvent and accumulation of cells at interphase<sup>32</sup> between the organic and aqueous layers.

In order to fix the problems associated with liquid-liquid extraction, pervaporation (vapor) and perstraction (liquid) have been developed. These techniques involve using a selective membrane, which is beneficial because proteins in cultures are often sensitive to heat or extractants. This process works by creating a chemical potential gradient which is usually induced by a vacuum, sweeping gas and/or temperature difference. One drawback with these two methods is that the membrane is a physical barrier that limits the extraction rate<sup>32</sup>. In pervaporation, the products are recovered by condensation

and a heat of vaporization is required as the feed temperature. Pervaporation removes products by a solution-diffusion mechanism where the selectivity of the membrane and the flux determine how much and fast the product is removed<sup>32</sup>.

Out of all of these techniques, the adsorption-desorption process has been proven to be easily the most economical at efficiently recovering butanol from a fermentation broth (Table 1)

Table 1. Values from<sup>33</sup> showing energy required for each technique; in context, the energy content of butanol is 7786.9 k cal kg<sup>-1</sup>

Separation Technique	Steam- Stripping Distillation	Gas Stripping	Pervaporation	Adsorption
Energy required (k cal kg <sup>-1</sup> )	5,789	5,220	3,295	1,948

Adsorption works by using solids with high internal surface area(500-1000m<sup>2</sup>/g) to physically attract solutes *via* van der Waals forces (modeled in fig.

2). Typical adsorbents include silica, resins, and activated charcoal. An ideal

adsorbent has to be quick, have a high capacity, have low cost and easily desorbs and regenerates. Silica is favorable for the ABE process because of its

ability to concentrate butanol and to be regenerated and reused. Activated charcoal can adsorb more than silica but does not desorb as well and does not adsorb acids well<sup>33</sup>. For the research that was done this summer during my REU, activated charcoal was chosen as an adsorbent because of its organic nature (could be made in biorefinery), while adsorption was chosen over pervaporation because a synthetic membrane is not desirable for a biorefinery process.

A problem that arises when using adsorption is how to efficiently desorb the products from the activated charcoal. Techniques to extract the products include pressure swing, purge gas stripping, displacement desorption (gaseous compounds at high pressure) or a thermal swing operation based on

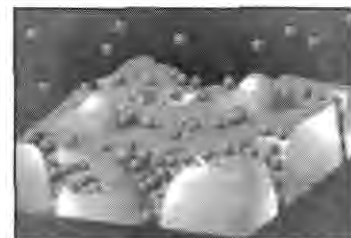


Figure 2. Model of Adsorption<sup>37</sup>; high surface area attracts solutes

the adsorption behavior as a function of temperature. However, only the last two of these are practical for the desorption of butanol because of its low vapor pressure<sup>33</sup>. In addition, liquid-liquid extraction has been shown to be the least energy intensive desorption process<sup>34</sup>.

Recent work has shown that an adsorption, drying, and subsequent desorption process has been effective in purifying butanol. This experiment was done using an aqueous 0.5 w/v butanol mixture and passing it through a column of silica crystals in powder form. Afterwards the crystals were taken out and dried to remove the moisture and then heated to 423 K where the butanol was desorbed and recovered by condensation. This process was able to recover 60-70% of the butanol with 98% purity<sup>38</sup>. A very similar process was tried with zeolite (silicate), where butanol was concentrated from 1.28 to 84.3 wt% with an 80% recovery<sup>39</sup>. Butanol, acetone, and ethanol were all desorbed by heat treatment (78°C) from a silicate in another experiment<sup>33</sup>. The results showed that the products were recovered at approximately 100, 95, and 80 percent of butanol, acetone, and ethanol, respectively. Another experiment was done where the concentration of butanol was able to be increased by a factor of 3 to 4, using methanol as a displacer to desorb acetone, butanol, and ethanol from a polyvinyl-pyridine resin. This process is favorable because of the low boiling point of methanol and the rapid desorption that occurs. This means that the process is easily reversible so the adsorbent can be reused<sup>33</sup>. Attempts have also been made to desorb butanol from bone charcoal. These experiments consisted of passing hot air (120°C) over the charcoal with adsorbed butanol. The exit air was then cooled to 0°C to condense the butanol. This resulted in a 60-65% recovery of butanol. Similar techniques were tried with resin; in these cases 75-85% of the butanol was recovered<sup>33</sup>.

## 2.4 Findings/ Discussion

A significant drawback of nearly all of the research done is that they focus on butanol, instead of utilizing all of the organic carbon produced from the fermentation. The research is also focused on butanol separation and purification because butanol is the desired product and is also the majority of the fermentation product. In the proposed process<sup>31</sup> to produce 'green' hydrocarbons all of the ABE major products are dehydrated/deoxygenated, not just butanol.

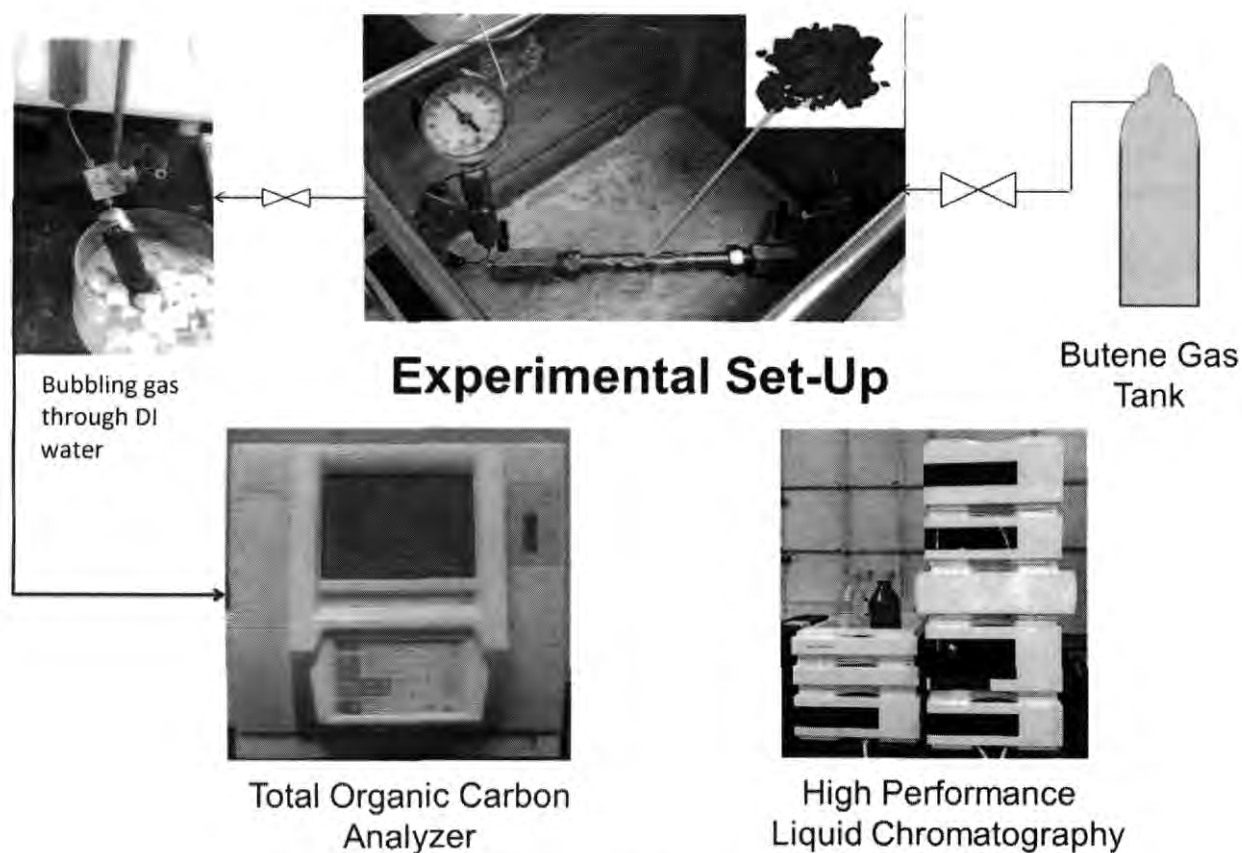


Figure 3. Diagram of experimental Set-up from REU, Summer 2013

Butene is the major gas produced by the catalytic conversion process of ABE products to hydrocarbons. Butene has very good properties for this process because under mild conditions (0°C & 25

psig) butene becomes a liquid, increasing its extractive ability. In these experiments, different temperatures (25&60°C), times (0.25, 1, 2, 4, 8, 24 hours), and concentrations (0.2 and 0.6 grams) were studied. Individual compounds were applied to determine the extractive power for each individual component.

As shown by the schematic above (fig. 3), acetone, butanol or ethanol were sprinkled (either 0.2 or 0.6 grams) onto 2 grams of activated charcoal which was then placed in a 10 ml tube. The tube was then sealed and connected to a butene tank (25 psig) and placed in an ice bath (0-5°C) for one hour to ensure that the butene in the 10 ml sealed tube was condensed. After an hour the connection to the butene gas tank was closed. The water in the tank was heated up (heating coil) and maintained at a specific temperature for a certain time mentioned in the above paragraph. After that time the tube was removed from the bath and the butene gas containing the acetone, butanol or ethanol was bubbled through 10 ml of cold deionized water. This sample was then run through a total organic carbon (TOC) analyzer. The parts per million of carbon was directly related to the amount of acetone, butanol or ethanol removed, as shown in the appendix. In addition another experiment was performed where the ABE products were put on the activated charcoal in a 3:6:1 ratio that would be found in a typical fermentation broth. They were extracted and analyzed by the TOC in the same procedure, and then run through a high performance liquid chromatography (HPLC) to determine the ratio the products would be extracted by butene.



## 2.5 Results

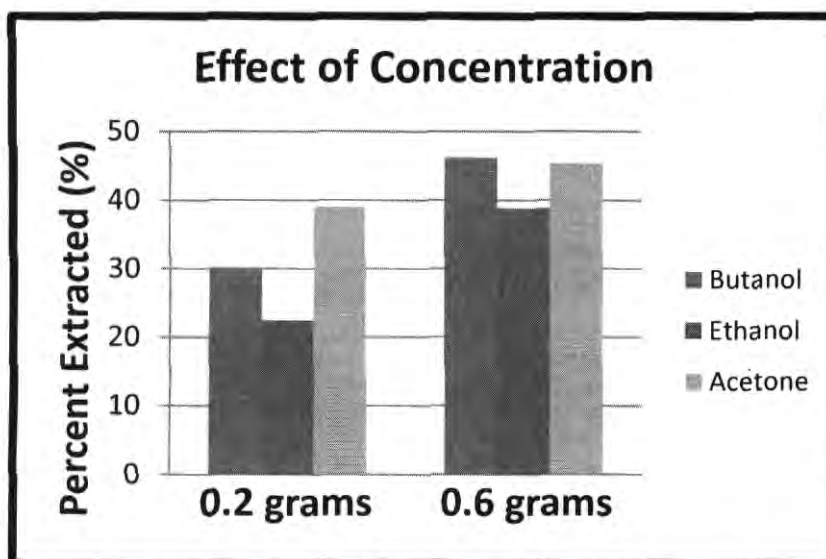


Figure 4. Percent extracted of 0.2 grams &amp; 0.6 grams for each solvent

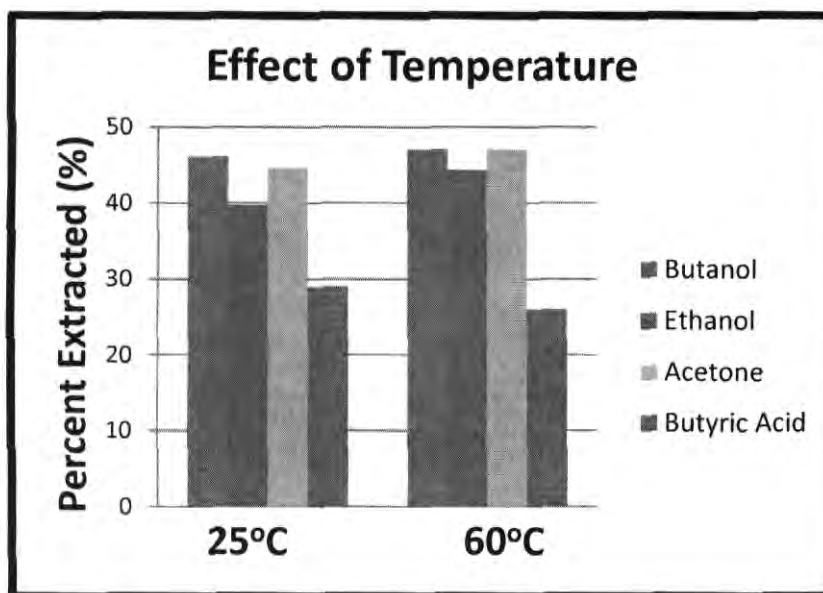


Figure 5. Percent extracted at 25°C &amp; 60°C for each solvent

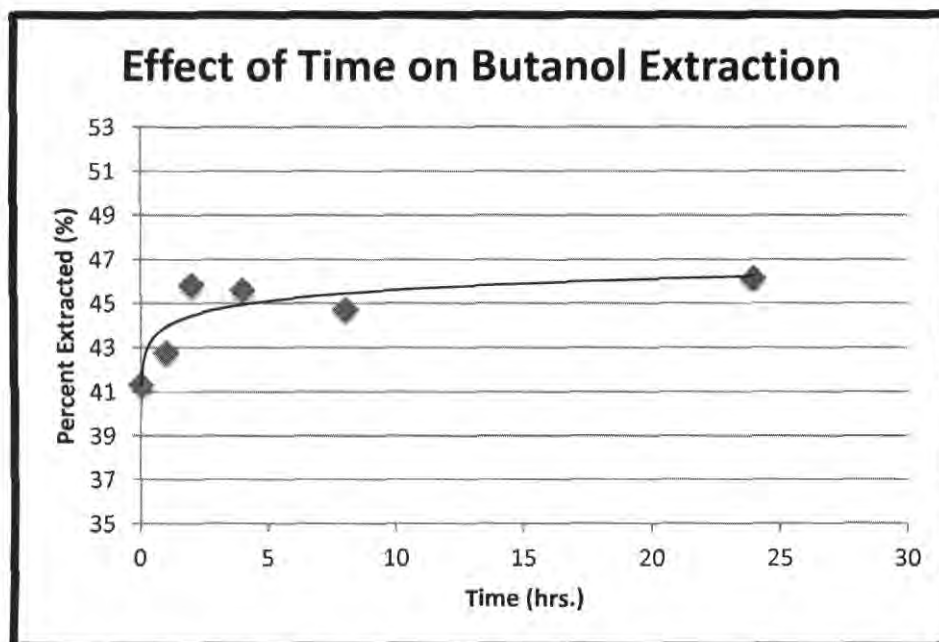


Figure 6 Time dependence of the percent of butanol extracted from activated charcoal

Table II. Amount of each product recovered in a model (3:6:1) fermentation broth, along with corresponding polarities.

	Peak Area	wt recovered (mg)	wt input (mg)	% Removed	Polarity Index
Butanol	81.73	256	389	66%	4.0
Acetone	26.15	70	183	38%	5.1
Ethanol	10.33	23	60	38%	5.2

The results showed that liquid butene extracted between 40-50% (fig. 5-7) of the major ABE components under the tested conditions, with 90% of the extraction occurring within the first 15 minutes (fig. 7). Increasing the concentration of the product on the activated charcoal (fig. 5) along with increasing temperature (fig. 6) was shown to improve the percent extracted. Phase equilibrium was reached within the first few hours, with 2 to 4 hours being the optimum time of extraction. When the ABE products were placed on the activated charcoal in the 3:6:1 ratio, HPLC showed that butanol was



preferentially extracted from the activated charcoal by liquid butene (Table 2). This is thought to occur because butanol is the least polar of the ABE products, having a polarity most similar to butene.

In the lab the butene gas was bubbled through 10 ml of DI water, while in future work and scale up, the process would use a mixture of the ABE products. The polarity index of the fermentation products are dissimilar to water, so in this process hopefully more products will be recovered. In order to do this in a commercial process you must already have product, so for start-up a condenser would be needed.

## 2.6 Implications

There is more work that must be done in the separation and purification of the ABE fermentation products to determine a method that is economically feasible. Qureshi, one of the foremost experts on butanol separation, says that future research should involve using silicates, since it was previously stated that silicate was the most effective at concentrating butanol<sup>33</sup>. Qureshi also notes that *Clostridium acetobutylicum* has a full cellulosome but does not have the genes to use it<sup>32</sup>. Work done in this area to add cellulosome-encoding genes can make it possible for *Clostridium acetobutylicum* to break down the cellulose structure. Qureshi also discusses that in a biorefinery, fermentation by-products such as CO<sub>2</sub> & H<sub>2</sub>, cell mass and large waste water streams could add further revenue<sup>32</sup>. The ABE fermentation process is widely agreed to be the best avenue for the renewable production of butanol, and many believe that the production of biobutanol using biomass is very close being scaled up<sup>32</sup>. This is very important if the US is serious about reaching the EISA goals.

The proposed catalytic conversion process<sup>31</sup> is based on a model fermentation broth with the products in a 3:6:1 ratio. The proposed process that uses activated charcoal and butene to

separate/purify the fermentation products changes this ratio, so work would need to be done to see if different parameters in the catalytic dehydration/deoxygenation would be necessary. Since butanol is in a higher fraction than previously studied, it is proposed that yield will be increased, since it contributes the most towards long chain hydrocarbon synthesis. Butyric acid, a minor product from the ABE fermentation, creates a significant problem that needs to be addressed. When butyric acid interacts with activated charcoal it is chemisorbed, as evidence by the white elongated crystals that were formed on the surface of the activated charcoal during the REU. This decreases the adsorption power of activated charcoal, so the ability to remove the small amount of butyric acid in the solution is needed. Future work in this area includes further optimization of temperature, time and amount of butene used for extracting. This work would include generating curves of activated charcoal and butene phase equilibria. Further work is also desirable on what can be used as adsorbents or catalysts to help increase the yield of the process and make the whole process more efficient and economical.



This work encompasses two studies at two different universities. Both studies were done with the aim to help improve biorefineries; either through expanding raw material for emerging biorefineries, or to develop a potential biorefinery process.

For a Biorefinery, wheat straw, a source of biomass, and the process developed to purify fermentation products containing butanol show potential. In the future, the work from each part could be combined in a biorefinery process. In comparison to hardwoods, higher dissolution and lignin removal of wheat straw *via* HWE, make it suitable for acid/enzymatic hydrolysis because of the lower amount of lignin-based inhibitors. These sugars could then be used by a *Clostridium* microbial strain to produce acetone, butanol and ethanol. These solvents could then be purified in the processes experimented with and catalytically converted to long-chain hydrocarbons.

### 3.1 Wheat Straw

Wheat straw has one of the greatest potentials of all agricultural residues because of wide availability and low cost. For wheat straw, pellets could potentially be made for CHP systems, or the carbohydrates could be broken down into sugars and used for fermentation.

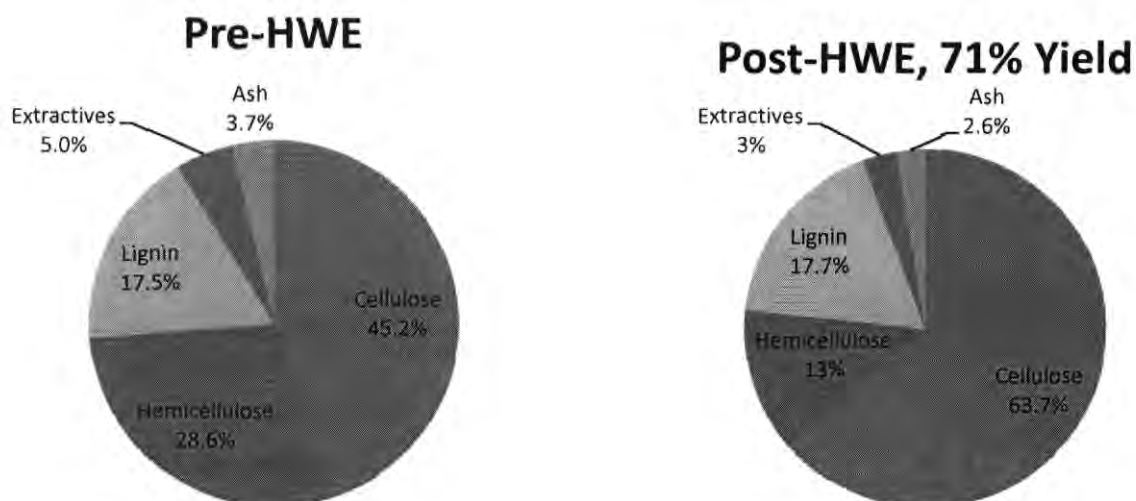


Figure 1. Chemical composition of wheat straw before and after Hot-Water Extraction

A few major conclusions can be made from figure 1. There is a large decrease in hemicelluloses, along with an increase of cellulose content, because very little to no cellulose was lost in the HWE. There is also 50% loss of ash which is very beneficial for pellet making.

An equation suggested from Demirbas shows a relation between heating value of biomass to the lignin content.<sup>30</sup>

MJ/kg	Equation	Actual
Pre-HWE	18.4	18.5
Post-HWE	18.4	19.1

$$(\text{MJ/kg})\text{HHV} = 0.0889(\%\text{lignin}) + 16.8218$$

Figure 2. Equation for HHV based on percent lignin<sup>30</sup>; HHV before and after HWE compared to values from equation

For the raw wheat straw sample it showed a very close correlation to the Demirbas equation. However, as shown in figure 2. the HHV does not increase as predicted from the equation for the Hot-Water Extracted wheat straw. The equation does not take into account large hemicellulose removal (shown in fig. 1), which is used to calculate the y-intercept. A new model for pretreated biomass will have to be determined based on a certain percentage of hemicellulose removal.

Compared to other monocotyledons tested (e.g. corn cobs 32%), the percent of lignin dissolved is very similar; and approximately double what many studies have found for sugar maple (~15%)<sup>41</sup>. This most likely has to do with the fact that monocotyledons have a more open structure and possibly lignin of lower molecular weight compared to hardwoods or softwoods, making it easier for the hot water to solubilize and remove the lignin. This is presented in Table I, where the density of the monocotyledons is shown to be less than that of hardwoods, including sugar maple. With the already porous structure of wheat straw, Hot-water extractions also increase porosity<sup>13</sup>, making the HWE extracted wheat straw open and readily accessible to acid/enzymatic hydrolysis. The hemicellulose loss was calculated using a mass balance; it was shown to be up to 74%, if nothing else was removed besides the lignin and ash that were tested for. This is quite high and is significant in other ways than just pellet making.

Table I. Densities of LCBs<sup>42</sup>

LCB type	Density (lb-ft <sup>3</sup> )
Wheat Straw	1.5
Corn Cobs	4
Hardwoods	22

The fact that the HHV does not increase significantly and that a large amount of lignin is removed compared to hardwoods shows that wheat straw would be better suited to be used as a feedstock to be converted in sugars for fermentation, and not pellets for CHP.

### 3.2 Purification of Fermentation Products

Ethanol has properties that do not make it viable as the major biofuel of the future.<sup>24</sup> Butanol has much better potential and large amount of research has been put into biobutanol from *Clostridium* microbial strain. The genetics have advanced significantly in the past 20 years, but upstream and downstream processes (pretreatment, separation/purification) still require major improvements before biobutanol production can compete with petrochemically derived butanol. An adsorption-desorption process has been shown to be the most energy-efficient way to purify the butanol. However most of the literature cited focuses on recovering butanol and not the other organic compounds produced by Acetone-Butanol-Ethanol (ABE) fermentation. Acetone and ethanol could both be sold individually, but the carbon produced by the fermentation could be used to make a higher value product. All three solvents can be extracted at 40% off the activated charcoal, showing that there is much more work that needs to be done to make this process more efficient.

A catalytic dehydration/deoxygenation process has been shown to be able to take the major ABE products and convert them into long chain hydrocarbons with comparable energy content to jet fuel. To reach the goal set by EISA, there must be a number of biofuels, from ethanol, butanol, diesel, and 'green' hydrocarbons in order to secure a future for the United States and the world. Biorefineries are essential to bring the lignocellulosic based economy to fruition.



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