HEMICELLULOSE AND CELLULOSE HYDROLYSIS FOR BUTANOL FUEL PRODUCTION

by

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Submitted in Partial Fulfillment of the Requirements

for the Degree of

Master of Science

in the

Civil Engineering

Program

YOUNGSTOWN STATE UNIVERSITY

May, 2013

Hemicellulose and Cellulose Hydrolysis for the Production of Butanol Fuel Production

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ABSTRACT

The process of extracting sugars from cellulosic materials in a high pressure and high temperature reactor was studied to maximize the production of sugars to use in the butanol fermentation process. The addition of chemicals was not used in this study; the components were wood based and water. The wood based materials used in the laboratory research were maple and sycamore. The research consisted of maximizing the amount of dissolved cellulosic material, by comparing the types of woods dissolved, comparing the temperatures and time at which the cellulosic material was dissolved, and recycling the liquor to maximize the amount of dissolved material. The laboratory research showed that the optimum combination of time and temperature needed to obtain the optimum dissolved material was 60 minutes at 250°C. It was also concluded that by recycling the liquor, the total dissolved solids for the three extraction runs was 18.85 grams, 53.96% of the solids were dissolved into the liquor.

ACKNOWLEGEMENTS

I would like to thank my advisor Dr. Douglas Price for his support and guidance, to help make it possible for me to complete this work. I appreciate his patience and time he contributed towards my work.

My special thanks to Dr. Scott Martin for all your great lectures from my undergraduate classes to my masters classes. I have enjoyed having you as a professor in all of my higher education work. I try to model my current work to how you presented in your lectures.

My special thanks to Professor David Kurtanich for his encouragement and support throughout my years associated with him at Youngstown State University.

I would be failing in my duty as a husband and father if I do not acknowledge the love and encouragement of my wonderful wife Angela Sanson and my daughters Olivia and Chelsea Sanson.

I would also like to acknowledge my late father Donald Sanson for stressing to me the importance of obtaining an education.

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CHAPTER 1 - INTRODUCTION

The increase in world population along with emerging industrial countries is beginning to put a strain on the world's fossil fuels. The industrialized nations are huge consumers of oil, coal, and natural gas.

Oil is considered irreplaceable, due to the millions of years needed to form oil deposits. Oil is formed from the bodies of single celled aquatic organisms. Oil is formed when the bodies of the aquatic organisms are entrapped in clays or other types of sediment. The organic matter is protected by the clay and transformed into a material called kerogen. The kerogen is covered with the deposition of sediment, increasing the distance the kerogen is from the surface of the earth. The more the distance the kerogen is from the surface of the earth, the pressures and temperatures are increased causing the formation of oil and natural gas. Oil is typically formed at depths of 2500 to 16,000 feet below the earth's surface (Tabak, June 2012).

The current oil reserve estimates, according to the journal article "The status of conventional world oil reserves – Hype or cause for concern?", are between 850 to 900 giga barrels (1 giga barrel = one billion barrels)(Owen, March 2010). Figure 1 indicates the projected world oil reserves and consumption from 2000 to 2100. The world currently withdraws approximately 86,954,000 barrels/day and consumes approximately 87,135, 100 barrels/day (U.S. Energy Information Administration, June 2012). Reports indicate, based on current consumption and current proved reserves, the future resource availability is 50 years. The United States consumes approximately 18,835,000 barrels/day; therefore Figure 1 indicates the forecasted oil reserves and oil consumption from 2000 to 2100 (Owen, Nick, March 2010).

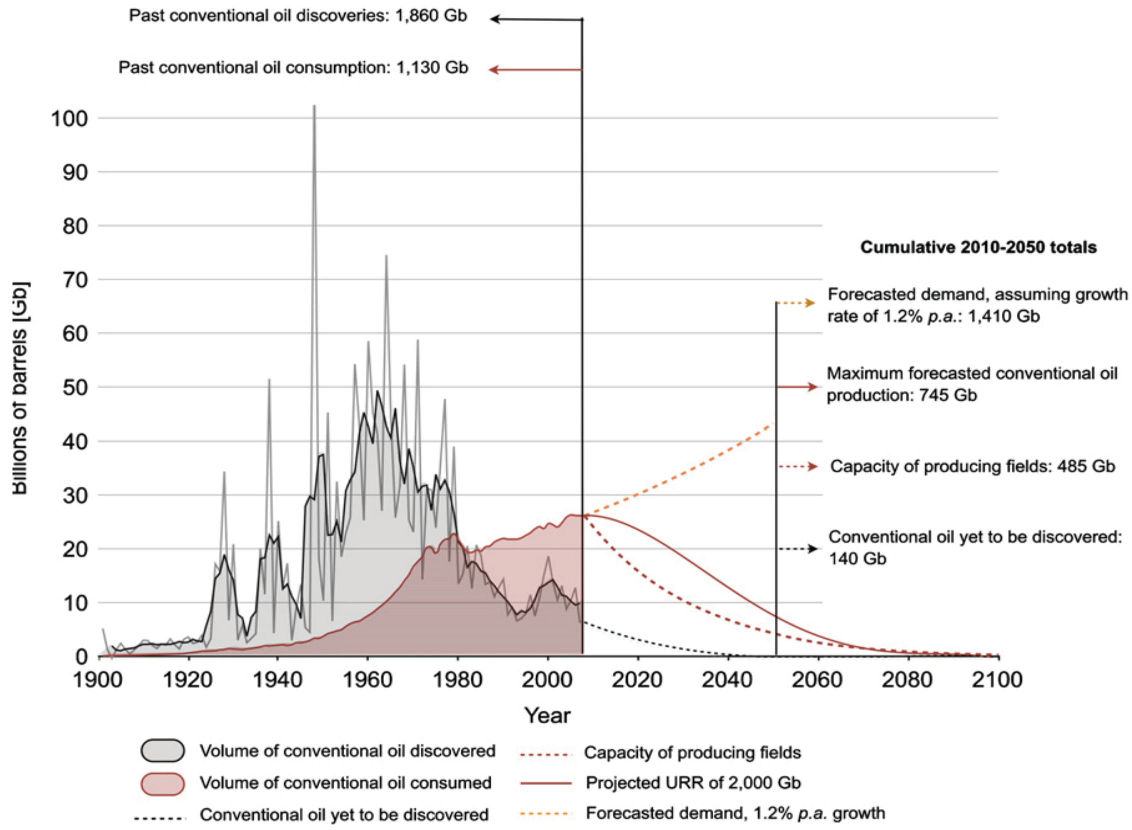

Figure 1: Annual backdated 2P conventional oil discovery, conventional oil consumption, and forecasted production and discovery **(Owen, March 2010).**

United States consumes approximately 21.6% of the world's oil. The United States imports 45% of the petroleum it consumes; its top supplier is Canada. Figure 2 indicates the major countries the United States imports oil from. The United States utilizes 71% of its oil consumption on transportation. Alternate fuels are urgently needed for transportation purposes in the near future.

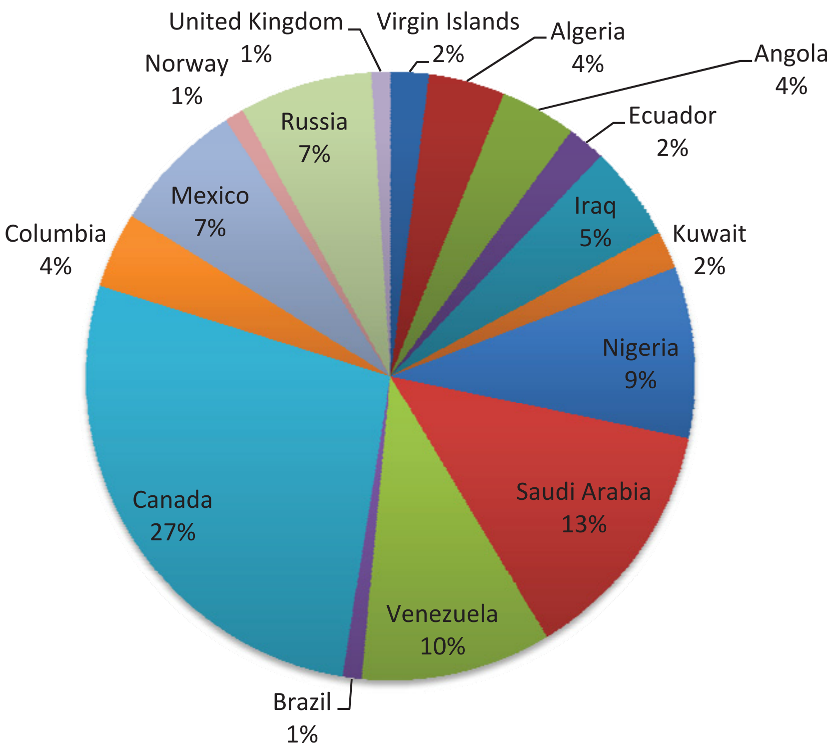

Figure 2: Top Countries U.S. Oil Imports: Source (U.S. Energy Information Administration, April 23, 2012)

Coal, like oil, is a non-renewable energy source because it takes millions of years to create. Coal is formed by dead plants that died in swamps millions of years ago and were covered by layers of water and soil, trapping the energy in the plants. Layers and layers of soil help create heat and pressure, which turn the dead plant material into coal. Coal is the most abundant fossil fuel in the United States. Coal is classified into four main types, anthracite, bituminous, subbituminous, and lignite. Anthracite contains 86-97% carbon, it is the least- mined in the United States, all of the anthracite mines are located in northern Pennsylvania. Bituminous coal contains 45-86% carbon and is the most abundant type of coal found in the United States.

Bituminous coal is used for electricity generation and in the steel and iron industry. Bituminous coal is mined in West Virginia, Kentucky, and Pennsylvania. Subbituminous coal has a lower heating value than Bituminous. Subbituminous coal contains 35-45% carbon; it is mined mainly in Wyoming. Lignite coal contains 25-35% carbon, is crumbly and has high moisture content. Lignite is mined in Texas and North Dakota (January 9, 2012, U.S. Energy Information Administration). The United States recoverable coal reserves is approximately 259.5 billion short tons (1 short ton = 2000 lbs). Based on the increased production of coal in the United States, the recoverable coal reserves will be exhausted in approximately 168 years. The total resources of coal is approximately 4 trillion short tons in the United States.

Natural gas is formed just as oil and coal; organic matters from millions of years ago get trapped beneath silt and sand, which changes to rock. The pressure and heat change the organic matter into oil, coal, and natural gas. The natural gas is methane, an odorless and colorless gas. According to the Energy Information Administration, Annual Energy Outlook 2011, the United States has 2,543 trillion cubic feet of potential natural gas resources, and continues to discover more each year. The United States is currently the top producer of natural gas. The United States natural gas reserves are estimated to last approximately 100 years. The United States produced 23 trillion cubic feet of natural gas in 2011 and consumed 24.4 trillion cubic feet. U.S. imported 3.4 trillion cubic feet of natural gas in 2011, Canada being the top supplier to the United States. Figure 3 shows the increased production and consumption of natural gas in the United States since 1949. The consumption and production of natural gas has been increasing since 1930. The United States has currently discovered recoverable natural gas in Marcellus and Utica Shale formations, with extraction through horizontal boring and a new hydraulic fracturing (fracking) process. Fracking is the process by which the shale formation is fractured by the use of explosives, the hydraulic fracturing fluids consisting of 90% water, 9.5% sand, and 0.5% chemicals, which are injected into the well under high pressure to extend and develop the fracture. The hydraulic fluids are then removed from the well (Intermountain Oil and Gas BMP Project, University of Colorado Law School, June 2012). The production of natural gas through fracking will increase natural gas production from 653 billion cubic meters (bcm) in 2011 to 769 bcm 2017 according to the Energy Information agency (Flynn, June 6, 2012).

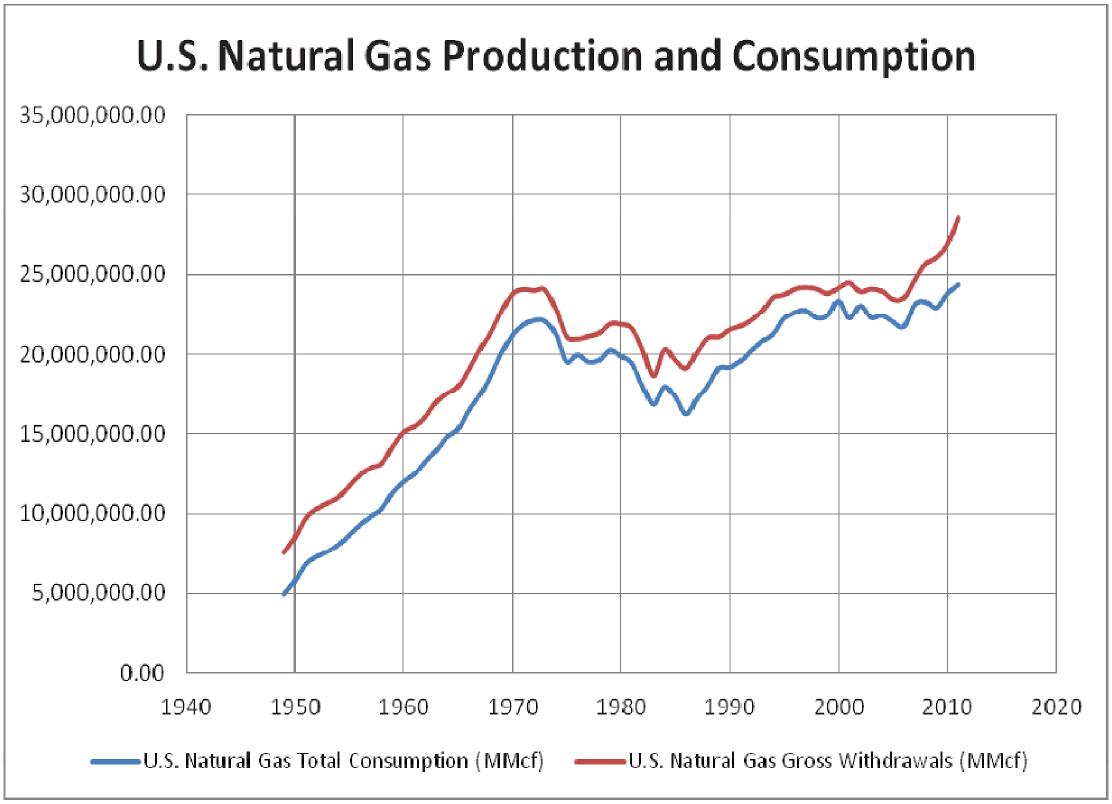

Figure 3: U.S. Natural Gas Production and Consumption **(**U.S. Energy Information Administration, May 31, 2012)

Gasoline is a product that is made from crude oil, through a distillation process. Gasoline is a volatile product and will vaporize at room temperature. Gasoline vaporizes more as the temperature increases, therefore gasoline are produced with different vapor pressures during the winter and summer months. Nineteen gallons of gasoline is produced from one 42 gallon barrel of oil,

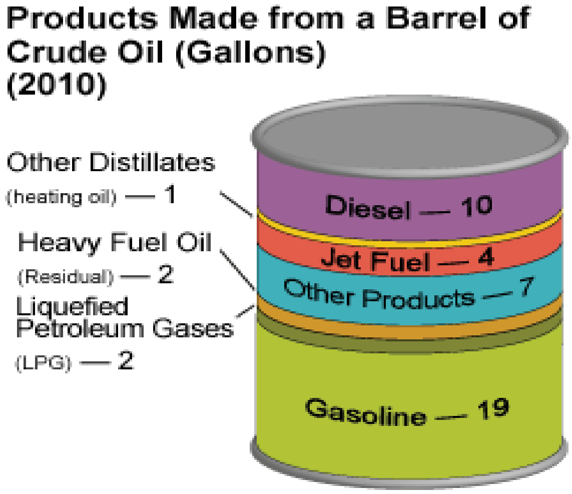

Figure 4: Products made from a Barrel of Oil **(**U.S. Energy Information Administration, June 17, 2011).

Gasoline is one of the major fuels consumed by the United States. In 2011, 131 billion gallons of gasoline was consumed, which is an average of 360 million gallons per day (April 12, 2012, U.S. Energy Information Administration).

1.1 Sustainable Energy

The needs for sustainable energy sources or renewable sources are greater than ever before. The present life of oil resources of approximately 50 years and the effect of coal on the environment currently are major factors necessitating production of an economically feasible renewable energy source for electricity and transportation. Sustainable energy sources that are currently in production and use are biomass, water (hydropower), geothermal, wind, and solar. Biomass energy sources consist of wood and wood waste, municipal solid waste, landfill gas, ethanol, and biodiesel.

Figure 5 represents the U.S. energy consumption by energy source in 2011. The United States consumed approximately 9 quadrillion Btu's in renewable energy. One gallon of gasoline equals approximately 124,238 Btu, so if the total 9 quadrillion Btu's were used in the form of gasoline, that would be approximately 72 billion gallons of gasoline, which would be 63% of our gasoline consumption in the United States.

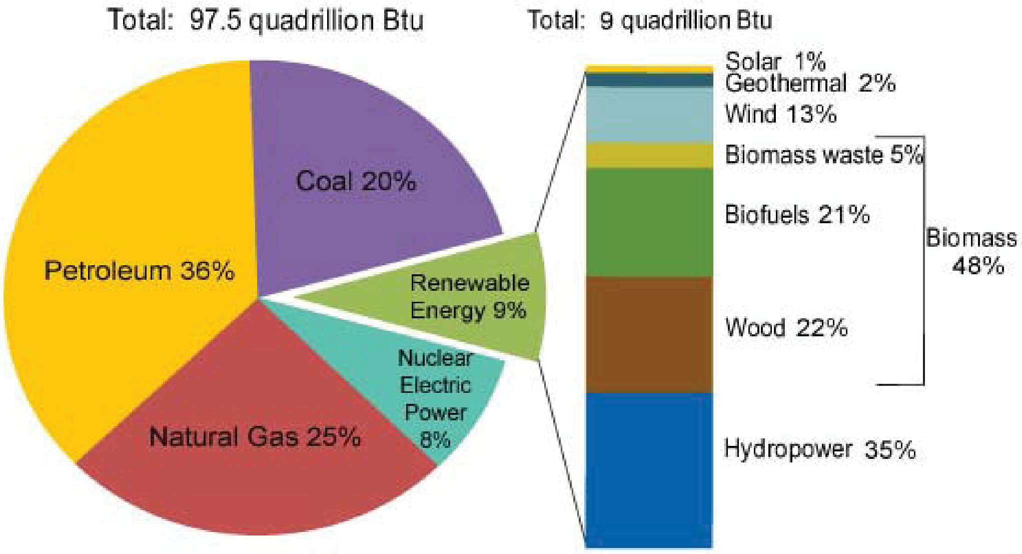

Figure 5: U.S. Energy Consumption By Energy Source **(**U.S. Energy Information Administration, March, 2012).

1.2 Bio-fuels

Currently the biofuels produced and consumed around the world are ethanol and biodiesels. Ethanol was first produced in the 1950's, and used as a fuel for lighting. In 1908, Henry Ford designed his Model T to run on a mixture of gasoline and alcohol. The use of ethanol has fluctuated over time due to different reasons. In 1919, Prohibition diminished the use of ethanol; because it was considered a liquor, it could only be sold when it was mixed with petroleum. Ethanol use increased during World War II due to the scarcity of oil and other resources. During the 1970's, the United States increased its use of ethanol as a transportation fuel due to rising oil prices and growing dependence on oil imports. The United States enacted the renewable fuel standard in 2005 that set minimum requirements for uses of renewable fuels. The renewable fuel standards will require the use of 36 billion gallons of renewable fuels by 2022. 13 billion gallons of ethanol were added to the gasoline consumed in the United States in 2011(April 16, 2012, U.S. Energy Information Administration).

The most common process used today is the production of ethanol. The starch in the corn is fermented into sugar, which is then fermented into alcohol, separated by distillation. Ethanol currently is also being produced by breaking down cellulose in woody fibers. The current processes use trees, grasses, and crop wastes. The use of cellulose reduces the need to use grains or other food stocks. Some of the positive aspects of ethanol are that it is non-toxic and biodegradable. Ethanol and ethanol gasoline mixtures burn cleaner and have higher octane than pure gasoline.

Biodiesel is made from vegetable oils, animal fats, or greases. Most biodiesel today is made from soybean oil. Biodiesel fuels can be used in diesel engines without any modifications.

Ethanol produced from feed stock such as corn and sugar is very controversial. The reason for the controversy is the very growing need to feed the world. The use of corn for the production of ethanol in 2010 consumed 30 percent of the United States' corn crops. The World Development Report estimates that the corn required to fill a sport utility vehicle one time with ethanol would feed one person for a year (World Development Report 2008).

1.2.1 Cellulosic Material

Ethanol is currently produced primarily from feed stocks such as corn and sugarcane. Cellulosic material such as wood, paper, cardboard, and fibrous materials, can be utilized in lieu of expensive feed stocks.

Cellulosic material is composed of lignin, hemicellulose, and cellulose; they are also referred to as lignocellulosic materials. Lignin is the component of the structure that gives the plant strength, and encloses the cellulose and hemicellulose. The lignin does not contain any sugars. Figure 6 shows a graphic description of a plant structure.

Cellulose consists of long chains of sugar molecules Hemicellulose is also comprised of long chains of sugar molecules, but in addition to glucose, contains

Table 1. The Characteristics of Selected Feed stocks and Fuels.

Characteristics of Selected Feedstocks and Fuels

		Cellulose (Percent)	Hemicellulose (Percent)	Lignin (Percent)	Extractives (Percent)
Bioenergy Feedstocks	Corn stover[a]	30 - 38	19 - 25	17 - 21	3.3 - 11.9
	Sweet sorghum	27	25	11	
	Sugarcane bagasse[a]	32 - 43	19 - 25	23 - 28	1.5 - 5.5
	Sugarcane leaves	b	b	b	
	Hardwood	45	30	20	
	Softwood	42	21	26	
	Hybrid poplar[a]	39 - 46	17 - 23	21 - 8	1.6 - 6.9
	Bamboo	41-49	24-28	24-26	
	Switchgrass[a]	31 - 34	24 - 29	17 - 22	4.9 - 24.0
	Miscanthus	44	24	17	
	Giant Reed	31	30	21	

Source:
Oak Ridge National Laboratory, Bioenergy Feedstock Development Program. P.O. Box 2008, Oak Ridge, TN 37831-6407 (compiled by Jonathon Scurlock in 2002, updated by Lynn Wright in 2008).

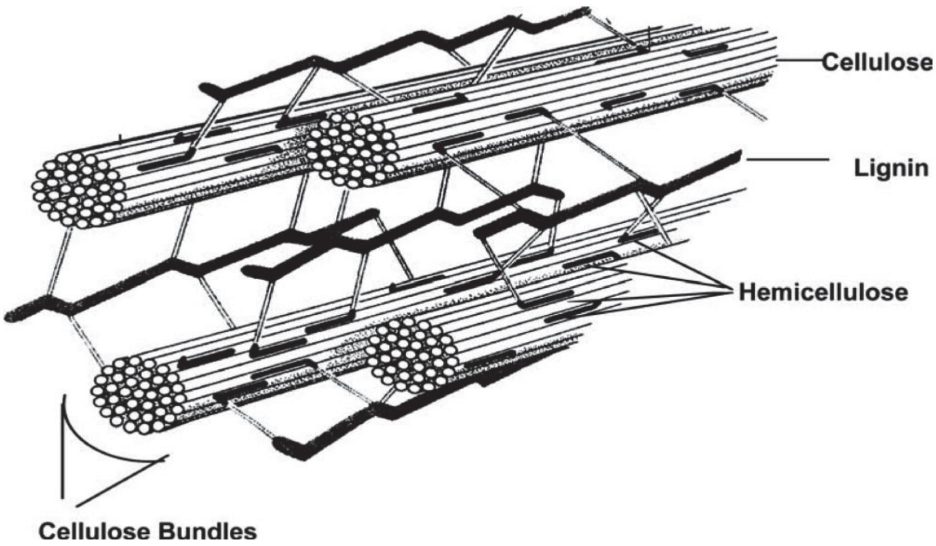

Figure 6. Typical plant cell-wall arrangement**.** (Yu et al., J*uly 6, 2007*)

pentose. Glucose is a 6-carbon sugar; pentose is a 5 carbon sugar. The hemicellulose can vary depending on the type of plant. (Badger, 2002). Table 1 presents the percentage of cellulose, hemicellulose and lignin in various feed stocks. Table 1 indicates that hardwoods have the highest percentage of cellulose and hemicellulose material amongst the most common feed stocks used in production of biofuels.

1.3 Ethanol vs. Butanol

Butanol resembles gasoline more than ethanol; butanol can replace gasoline in a vehicle 100 percent. Butanol has an energy density closer to gasoline than does ethanol. Butanol has a lower chance of separation and corrosion than ethanol.

Butanol resists water absorption, allowing it to be transported in pipes and carries used for gasoline.

The website butanol.com provides some significant arguments as to why butanol would be a better alternative than ethanol. Butanol has an energy value of 110,000 Btu/gal, similar to gasoline (114,000) and much higher than ethanol (76,100). Butanol can be blended up to 40% with diesel fuel. Butanol reduces hydrocarbon emissions by 95%; carbon monoxide to 0.01%; and oxides of nitrogen by 37%. Butanol can be made from a wide variety of non-food feedstocks such as wood and forest residues (www.butanol.com).

The cost of producing butanol through the use of wood chips was described in an example, published by Xylene Power Ltd. (www.Xylene power.com/biofuels.htm). The example takes in to account the cost of debarking lumber and reducing the wood into wood chips. The follow calculation involves using a raw material as an example, not a waste product that could be obtained from other processes.

The cost of reducing the wood into wood chips is $118/ton. The moisture content of the wood is 40%; therefore the cost of contained dry carbohydrate is $118/800 lbs. The maximum theoretical yield of butanol from the dry carbohydrate is given by:

$$0.30\ x\ 800\ lb = 240\ lbs.$$

The cost of feed stock alone for making butanol using an ideal process is given by:

$$\frac{\$118}{240 lbs\ butanol} = \frac{\$0.50}{lb\ butanol}$$

The density of butanol is 50 lbs/ft^3.

The energy density of butanol = 104,830 Btu/gal.

The present cost of delivered gasoline is $2.72/gal (no taxes or retail markup).

The density of gasoline is 6.073 lb/gal, so the cost of gasoline therefore is:

$$\frac{\$2.7.2}{gal}\ x\ \frac{1\ gal}{6.073\ lbs} = \frac{\$0.48}{lb}$$

The energy content = 114,000 Btu/gal.

The cost of feedstock required to make sufficient butanol to produce sufficient to replace 1 gallon of gasoline is:

$$\frac{50\ lb}{ft^3}\ x\ \frac{0.134 ft^3}{1 gal} = \frac{6.70\ lb}{gal}\ of\ butanol$$

$$\frac{114{,}000 Btu}{1\ gal\ gasoline} x \frac{1\ gal\ butanol}{104{,}830\ Btu}\ x\ 6.70\ lb\ butanol = 7.29\ lb\ butanol$$

$$7.29 lb\ butanol\ \ x\ \frac{\$0.50}{lb\ butanol} = \frac{\$3.64}{gal. equiv. butanol}$$

It would cost $3.64/gal to produce butanol equivalent to 1 gallon of gasoline. Therefore at the present cost of gasoline delivered at $2.72 and butanol at $3.64, butanol costs $0.92 per gallon more. The cost could be reduced by utilization of waste or a byproduct of some source, such as sawdust from a saw mill, as a feedstock. The above calculation utilizes a raw material that is specifically ground up for the production of butanol, if a waste product could be obtained at a zero cost or even at half the cost, $.25/lb. of butanol. The cost of butanol would be approximately $1.70/ gallon, which would be very feasible.

1.4 Purpose of Study

The research concentrated on maximizing the concentration of the cellulose and hemicellulose, through a physical process of removing the lignin to obtain all the maximum amount of sugars that could be used in the fermentation process. The maximum dissolved cellulosic material was determined by comparing the types of woods dissolved, comparing the temperatures and the extraction time at which the cellulosic material was dissolved, and recycling the liquor to maximize the amount of dissolved material.

CHAPTER 2 – REVIEW OF RECENT RESEARCH

A review of recent studies was performed to compare the laboratory results for this thesis with studies that have previously been performed. Two particular papers were reviewed, Water-Based Woody Bio Refinery (Thomas E. Amidon and Shijie Liu, 2009), and Some Recent Advances in Hydrolysis of Biomass in Hot-Compressed Water and Its Comparisons with Other Hydrolysis (Yu et al., 2008).

The paper titled Water-Based Woody Bio refinery, discusses the extraction of sugars from lignocellulosic materials and the percentage of dissolved woody materials. Amidon and Liu determined that hot water extraction at 160°C for 2 hours removed approximately 23% of the woody biomass. The extraction liquor pH. decreased increasing with extraction time and leveled off 1 hour after the desired extraction time was reached. The total measured dissolved solids in the extract increased with increasing extraction time. Xylose was the major component of the wood extract sugars. Figure 7 indicates the percent of mass removed based on time and temperature. Amidon and Liu found that as the temperature and extraction time increased the percent removal of wood increased. Amidon's research kept the temperature in the range 160-180°C.

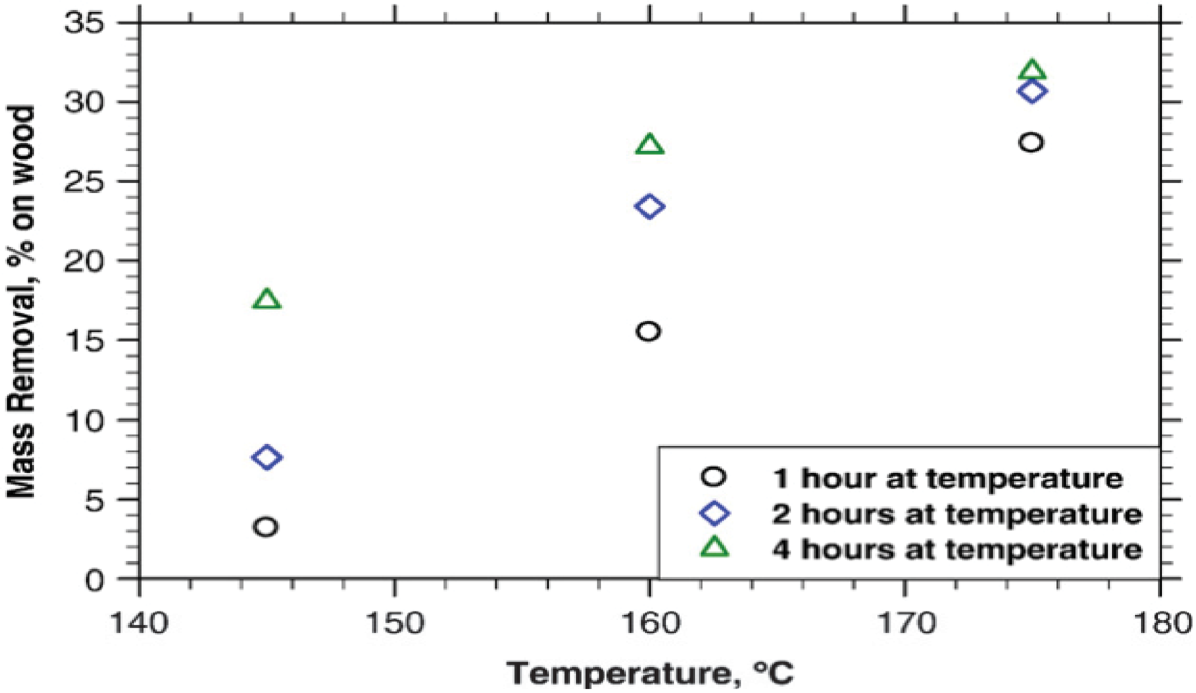

Figure 7.
Effect of extraction temperature on mass removal for sugar maple wood chips The experimental data were collected using a 6-l M/K® digester and the water:wood chip ratio was 5.92:1. Source (Thomas E. Amidon and Shijie Liu, 2009)

Yu's paper, discusses the temperature and time associated with the solubilize of hemicellulose and cellulose. When woody and herbaceous biomass was heated and compressed for 0 to 15 minutes at 200-300°C, 40-60% of the sample was solubilized. All cases studied showed that 100% of the hemicellulose was solubilized. The study showed that decomposition of hemicellulose starts at a lower temperature (180°C) than that of cellulose (230°C) and glucose rapidly degrades as the temperature increases to >230°C.

Yu et al. (2008) determined that the optimum conditions for biomass decomposition involve a two-step system. To obtain high sugar yield, a continuous flow-type reactor was favored, and a hydrolysis products needed to be cooled rapidly to minimize further degradation of sugars. Yu et al. determined that the approach is to recover the hemicellulose derived sugars first at 180-200 °C, then continue the process and increase the temperature to 230°C to obtain the glucose from the remaining solid residue. Yu et al. also determined that high sugar yields improved when the exposure to high temperatures were minimized.

Yu's study was able to obtain 95% dissolution of willow through a two stage continuous flow reactor. The glucose recovery was only 20%.

Both studies concurred that optimum temperature to achieve the maximum dissolved solids is 180-200°C.   Amidon's study concentrated on the amount of time required at certain temperatures to obtain the maximum dissolved solids. Yu et al. study concentrated on the maximum obtainable sugars, which he concluded to be at the lower range of 0-15 minutes. Yu et al. also determined that at a temperature over 230°C the sugars would start to degrade.

CHAPTER 3- METHODS

3.1 Materials

The objective of this research was to determine the maximum amount of dissolved solids that can be obtained from biomass hydrolysis in hot water, without the use of chemicals. Materials utilized for the research, as well as the information on the physical set-up of the process, and the method followed are detailed below.

3.1.1 Biomass

The biomasses that were utilized in the laboratory were samples of maple tree shavings and sycamore tree shavings. The maple tree shavings were obtained from a tree removal company located in the Youngstown area and the sycamore tree shavings were obtained from a tree removal project on the campus of Youngstown State University. The samples were sieved using a U.S.A. Standard Testing Sieve No. 16. The material that passed through the No. 16 Sieve was then placed into a grinder that ground the wood shavings into powder consistency.

3.1.2 Reactor Design

The reactor that was utilized to provide the hydrolysis of the biomass in hot water consisted of a steel vessel, 6.500 inches high, 2.496 inches inside diameter, and 0.267 inches thick, a lid, a mixing device, and a heating element. The lid of the reactor consisted of four pieces that extend from the inside of the cap that fits down inside of the vessel. The four pieces include a mixing paddle, copper tubing for cooling of the liquid inside the vessel, a thermocouple, and a pressure relief valve. The top of the lid consists of the gear required to rotate the mixing paddles inside the vessel, two ports that serve as an intake valve for providing cooling water that circulates through the copper tubing inside the vessel and a port that expels the circulating water to a drain, two smaller ports attached to the collar of the mixing gear to provide cooling water to the collar to prevent overheating of the mixing mechanism, a plug attached to the lid that is connected to the thermocouple for measuring the internal temperature of the mixture, a pressure relief valve attached to the lid, and a gauge to measure the internal pressure of the vessel. The vessel is heated to the required temperature by the use of a heating mantle. The heating of the reactor is controlled by a dial that is connected to the thermocouple. The heating is varied using a temperature controller. The vessel lid attached through the use of a two piece metal collar that is bolted on with six hex-head bolts. The two piece metal collar is then fitted with another one piece metal collar that holds the two pieces together with one hex-head bolt. A separate piece of the reactor is the mixing device that attaches to the mixing gear on the lid of the reactor. A variable-speed controller is used to vary the mixing rate and the speed is displayed by a strobe meter. Figures 8, 9, 10, and 11 represent the pieces of the reactor.

Figure 8. Reactor Apparatus Setup.

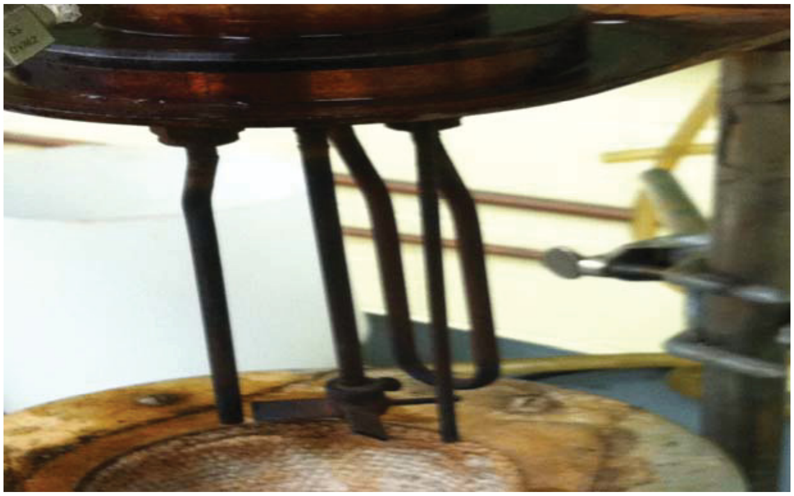

Figure 9. Inside Lid Mechanisms.

Figure 10. Outside Lid Mechanisms.

Figure 11. Vessel Cap Collars.

3.2 Experimental Method

A two-step experimental process was used. The dried wood must be put through a low heat process before the material can be put through the final hydrolysis process. Figure 12 provides a flow chart of the experimental procedure used in this work. A step- by-step explanation of the experimental procedure follows in sections 3.2.1 and 3.2.2.

3.2.1 First Stage - Low Heat Process

1. 320 ml of de-ionized water was placed into the pressure vessel.
2. 40 grams of dry ground up wood that passes through a U.S.A. Standard Testing Sieve No. 40 was placed in the pressure vessel.
3. The mixture in the vessel is heated to approximately 160°C for thirty minutes.
4. The vessel and mixture were cooled through the use of the water that circulates inside the vessel.
5. The cooled mixture was then filtered through a Whatman 12.5 cm diameter filter paper .
6. The filtered material (pulp) was stored in plastic storage bags and refrigerated, until use in the hydrolysis process.
7. The moisture content of the pulp material is determined.

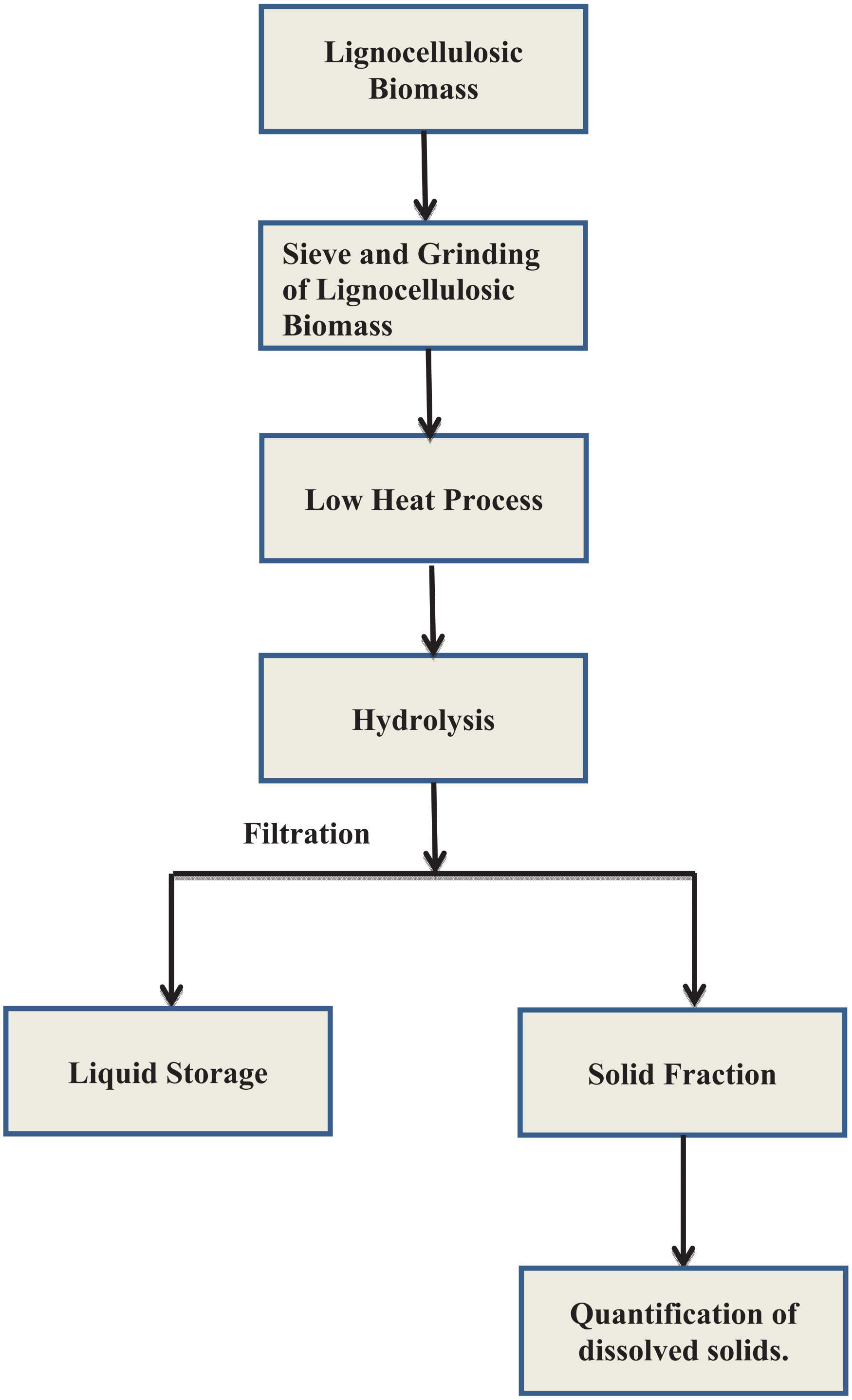

Figure 12. Flow chart of the experimental procedure.

3.2.2 Hydrolysis Process

1. 320 ml of de-ionized water was placed into to the pressure vessel.
2. 25 to 40 grams of wet pulp is weighed out on an electronic balance and recorded, then added to the pressure vessel.
3. The pressure vessel lid is then tightly bolted onto the vessel to obtain a tight seal.
4. The pressure vessel is then placed into the apparatus, and the heating element, mixing rod, and water circulation tubing is attached to the pressure vessel.
5. The heating element is then set to the desire temperature for the particular test.
6. The starting time is recorded at the time the heat is initially applied. The apparatus mixes the solution constantly as the desired temperature is reached.
7. The time at which the desired temperature is reached is recorded and the pressure at the desired temperature is recorded. The desired temperature is held constant for the required time limit for the particular test . The heating element is turned off when the time limit has expired and the cooling water is circulated though the outside of the vessel to cool it off.
8. The pressure is then released when the vessel has cooled down and the lid of the pressure vessel is then removed.

9. The weight of a new piece of filter paper is measured and recorded and placed in the funnel. The liquid from the vessel is then poured into the funnel, where the remaining pulp is collected on the filter paper and the liquor is collected in a beaker.
10. The liquor is stored for use in the fermentation process.
11. The filter paper and pulp is then weighed and recorded and then placed in an oven at 200 ° C to dry out the pulp.
12. The filter paper and pulp is then removed from the oven and weighed again, to determine the amount of dissolved solids in the liquor.

CHAPTER 4 - RESULTS AND DISCUSSION

In this study, various parameters like temperature, time, and recycle of liquor were examined to identify the maximum dissolved solids of a lignocellulosic biomass that could be obtained. The results are expressed in percentage of biomass dissolved. A 10% dissolved biomass yield means 1g of biomass was dissolved into the liquor per 10 g of oven dried pulp. The cellulosic biomasses that were analyzed were maple and sycamore wood chips.

4.1 Maple Lignocellulosic Biomass Extraction at 230°C

The results of the percent of the maple biomass dissolved in the water at a temperature of 230°C and times of 15, 30, and 60 minutes are shown in Table 2. The results show the maximum dissolved solids occurred at a time of 60 minutes.

Table2. Percent maple biomass dissolved in solution at 230°C.

Dry mass of pulp sample = 18.23%

Time at Temp. (min)	Wet Pulp (g)	OD Pulp (g)	H2O in Pulp (g)	H2O Added (mL)	Total H2O (mL)	Dried Pulp (g)	Pulp Dissolved (g)	% Dissolved
15	28.02	5.11	22.91	320	342.91	3.80	1.30	25.53%
30	28.00	5.10	22.90	320	342.90	3.51	1.59	31.17%
60	28.01	5.11	22.91	320	342.91	3.08	2.02	39.60%

The increase in dissolved maple lignocellulosic at a constant temperature of 230°C is shown in Figure 13. The amount of dissolved material increased 14.07 percent over 45 minutes.

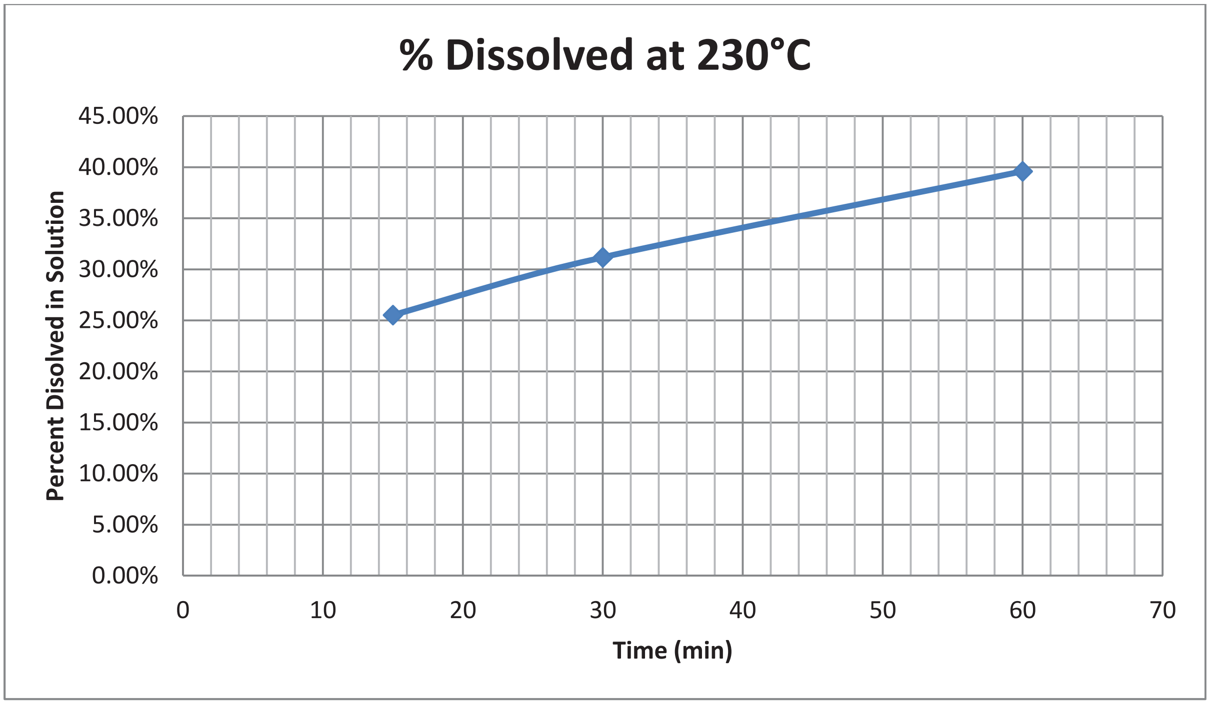

Figure 13. Maple lignocellulosic biomass extraction at 230°C at measured times of 15, 30, and 60 minutes.

4.2 Maple Lignocellulosic Biomass Extraction at 250°C

The results of the percent of the maple biomass dissolved in the water at a temperature of 250°C and times of 15, 30, and 60 minutes are shown in Table 3. The results show the maximum dissolved solids occurred at a time of 60 minutes.

Table3. Percent maple biomass dissolved in solution at 250° C.

Time at Temp. (min)	Wet Pulp (g)	OD Pulp (g)	H2O in Pulp (g)	H2O Added (mL)	Total H2O (mL)	Dried Pulp (g)	Pulp Dissolved (g)	% Dissolved
15	29.23	5.33	23.90	320	343.90	2.68	2.65	49.73%
30	39.45	7.19	32.26	320	352.26	3.06	4.13	57.46%
60	28.00	5.11	22.90	320	342.90	1.81	3.30	64.62%

The increase in dissolved maple lignocellulosic at a constant temperature of 250°C is shown in Figure 14. The amount of dissolved material increased 14.89 percent over 45 minutes. Figures 13 and 14 prove that the amount of dissolved material increases as the time of hydrolysis increases.

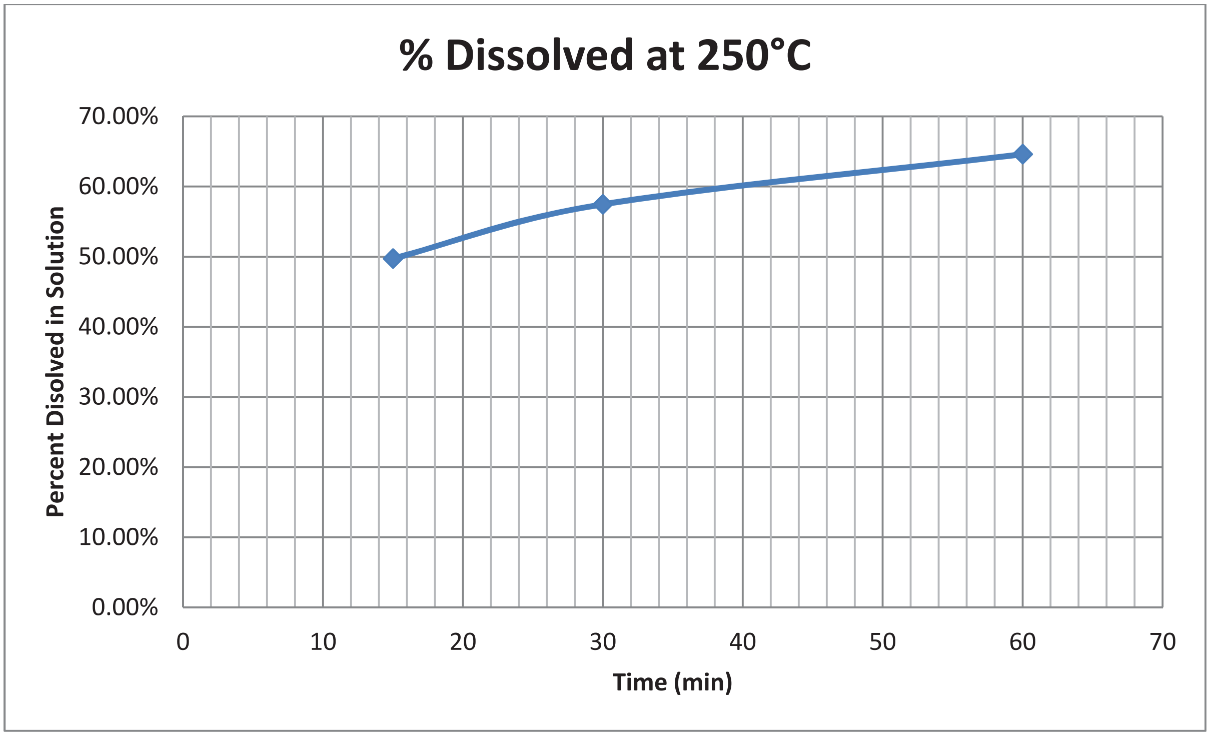

Figure 14. Maple lignocellulosic biomass extraction at 250°C at measured times of 15, 30, and 60 minutes.

4.3 Maple Lignocellulosic Biomass Extraction at Various temperatures at a Constant Time of 15 Minutes.

Data were collected from maple lignocellulosic biomass at various temperatures and a constant time of 15 minutes of extraction time were investigated for temperatures of 227, 230, 235, and 250°C. Figure 15 indicates that as the temperature is increased and the extraction time held constant at 15 minutes the amount of dissolved solids increases. There is an increase in dissolved solids of approximately 29%, with an increase in temperature of twenty-five degrees.

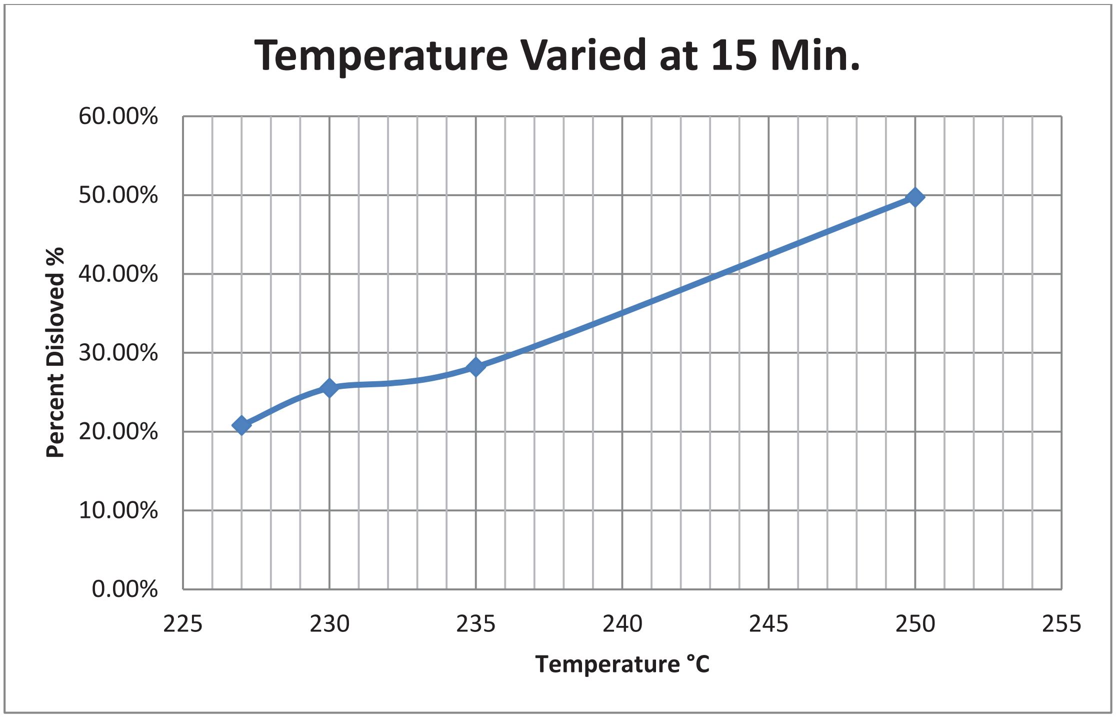

Figure 15. Maple lignocellulosic biomass extraction at various temperatures at 15 minute extraction.

4.4 Maple Lignocellulosic Biomass Extraction at Various temperatures at a Constant Time of 30 Minutes.

Data were collected from maple lignocellulosic biomass at various temperatures and a constant time of 30 minutes of extraction time were investigated for temperatures of 225, 230, 235, and 250°C. Figure 16 indicates that as the temperature is increased and the extraction time held constant at 30 minutes the amount of dissolved solids increases. There is an increase in dissolved solids of approximately 33 %, with an increase in temperature of twenty-five degrees.

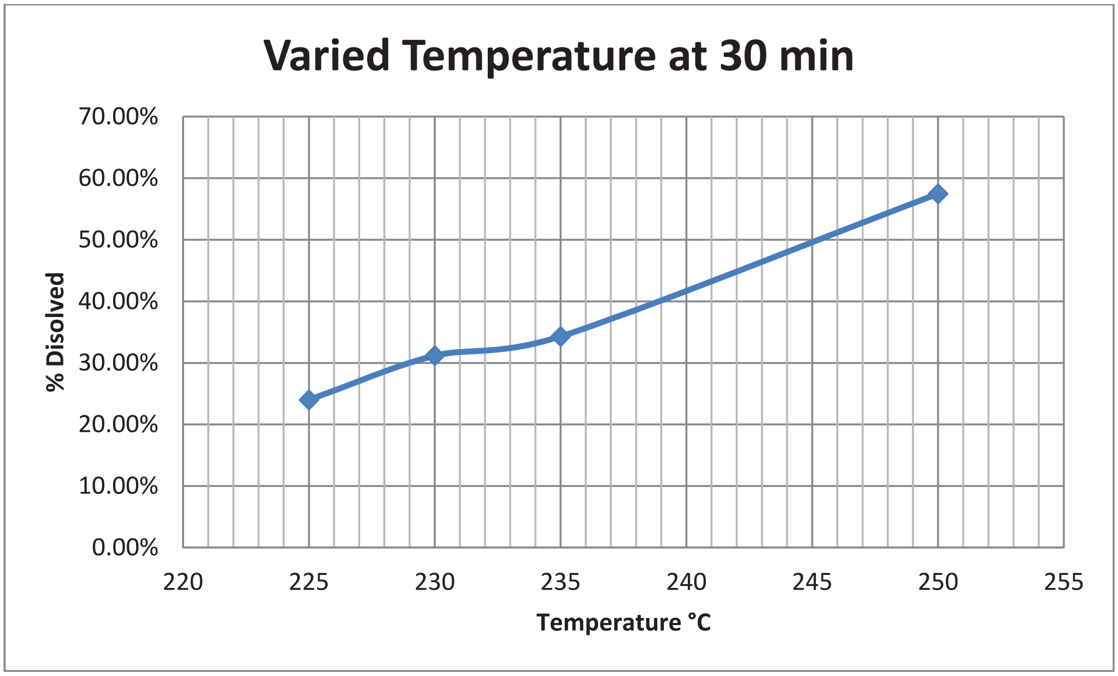

Figure 16. Maple lignocellulosic biomass extraction at various temperatures at 30 minute extraction.

4.5 Maple Lignocellulosic Biomass Extraction at Various temperatures at a Constant Time of 60 Minutes.

Data were collected from maple lignocellulosic biomass at various temperatures and a constant time of 60 minutes of extraction time were investigated for temperatures of, 230, 235, and 250°C. Figure 17 indicates that as the temperature is increased and the extraction time held constant at 60 minutes the amount of dissolved solids increases. There is an increase in dissolved solids of approximately 20 %, with an increase in temperature of twenty.

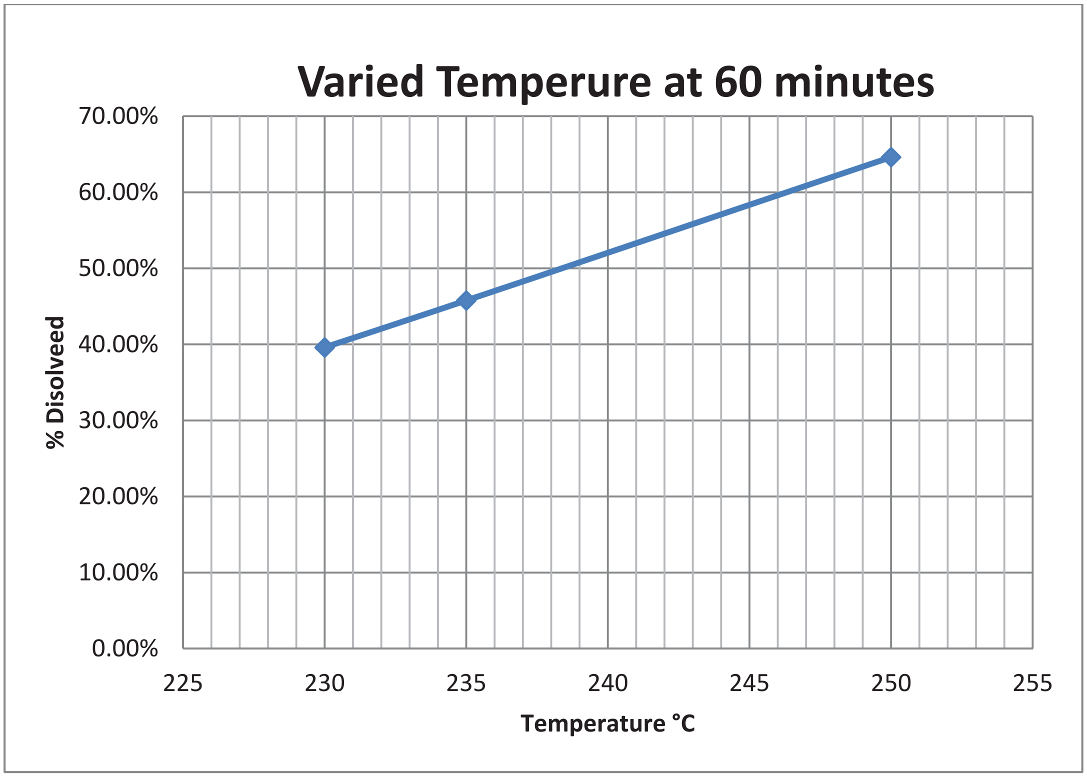

Figure 17. Maple lignocellulosic biomass extraction at various temperatures at 60 minute extraction.

4.6 Summary of Maple Lignocellulosic Biomass Extraction at Various temperatures at a Constant Times of 15, 30, and 60 Minutes.

Figure 19 indicates a summary of the maple lignocellulosic percent dissolved at various temperatures at constant extraction time. Figure 18 indicates two parameters, the maximum dissolved solids occurred at a temperature of 250°C at each extraction time and at 60 minutes the maximum percent dissolved solids occurred. The higher the temperature and the longer the extraction time provided the maximum dissolved solids.

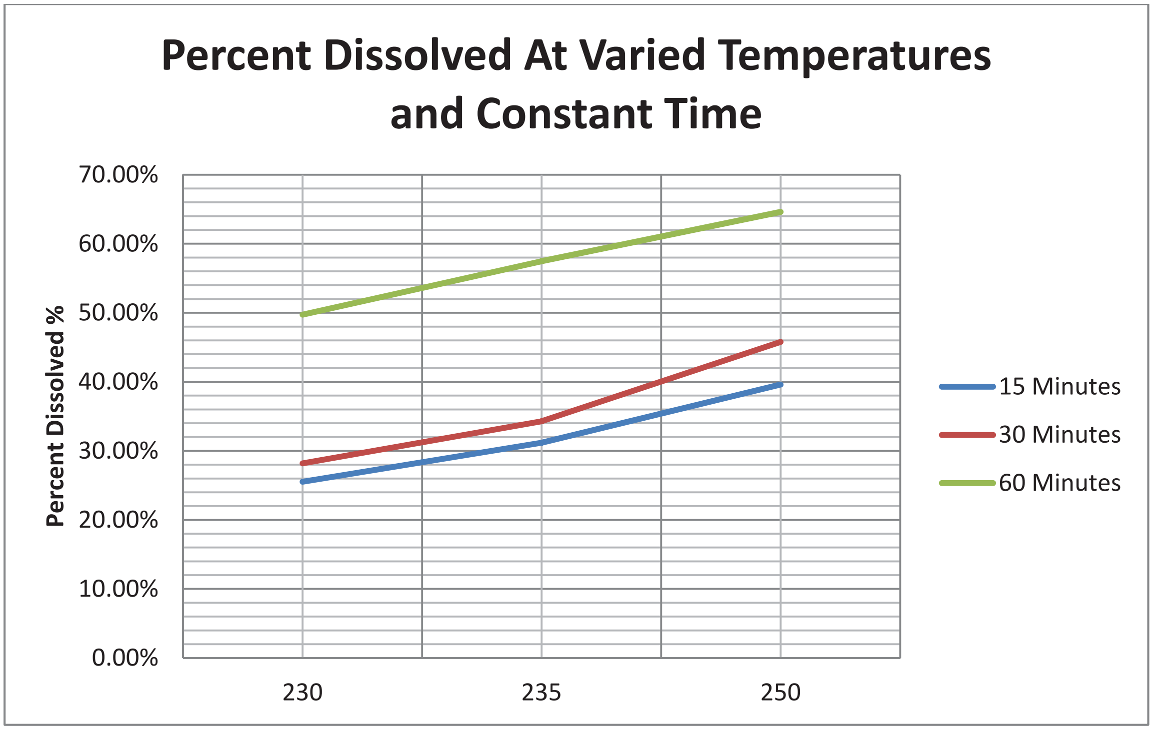

Figure 18. Maple lignocellulosic biomass extraction at various temperatures at 30 minute extraction.

4.7 Sycamore Lignocellulosic Biomass Extraction at a Constant Temperature of 260°C, at a Constant Time of 15 Minutes and The Liquor Recycled.

Sycamore lignocellulosic biomass samples were prepared and extracted at a temperature of 260°C and maintained at the temperature for 15 min. to measure the amount of solids dissolved. Three extraction runs were performed with sycamore lignocellulosic biomass at a temperature of 260°C and an extraction time of 15 min. The liquor from each of the extraction runs was recycled in the next extraction run, to measure the increase or decrease of solids dissolved.

A sycamore lignocellulose biomass sample was prepared, consisting of 11.13 g of wet pulp with a moisture content of 23.95% and 320ml of deionized water was added. The mixture was heated to a temperature of 260°C and maintained for 15 minutes. The initial dried pulp based on the moisture content of 23.95% was 8.46 grams, at the completion of the 15 minute hydrolysis, after filtration, and drying of the filtrate the remaining dried pulp was 3.878 grams. The calculated percent dissolved lignocellulose was 54.17%.

A second sycamore lignocellulose biomass sample was prepared, consisting of 21.14 grams of wet pulp. With a moisture content of 23.95%, 300ml of recycled liquor and an addition of 20 ml of deionized water. The mixture was heated to a temperature of 260°C and maintained for 15 minutes. The initial dried pulp based on the moisture content of 23.95% was 16.08 grams, at the completion of the 15 minute hydrolysis, after filtration, and drying of the filtrate the remaining dried pulp was 6.94 grams. The calculated percent dissolved lignocellulose was 56.81%.

A third sycamore lignocellulose biomass sample was prepared, consisting of 11.46 grams of wet pulp. With a moisture content of 23.95%, 280 ml of recycled liquor and an addition of 40ml of deionized water. The mixture was heated to a temperature of 260°C and maintained for 15 minutes. The initial dried pulp based on the moisture content of 23.95% was 10.40 grams, at the completion of the 15 minute hydrolysis, after filtration, and drying of the filtrate the remaining dried pulp was 5.27 grams. The calculated percent dissolved lignocellulose was 49.38%.

Figure 19 indicates an increase in solids dissolved when recycling 300 ml of liquor in the second extraction run and a decrease in solids dissolved when the liquor was recycled a second time. The total solids dissolved for the three extraction runs was 18.85 grams, 53.96% of the solids were dissolved into the liquor.

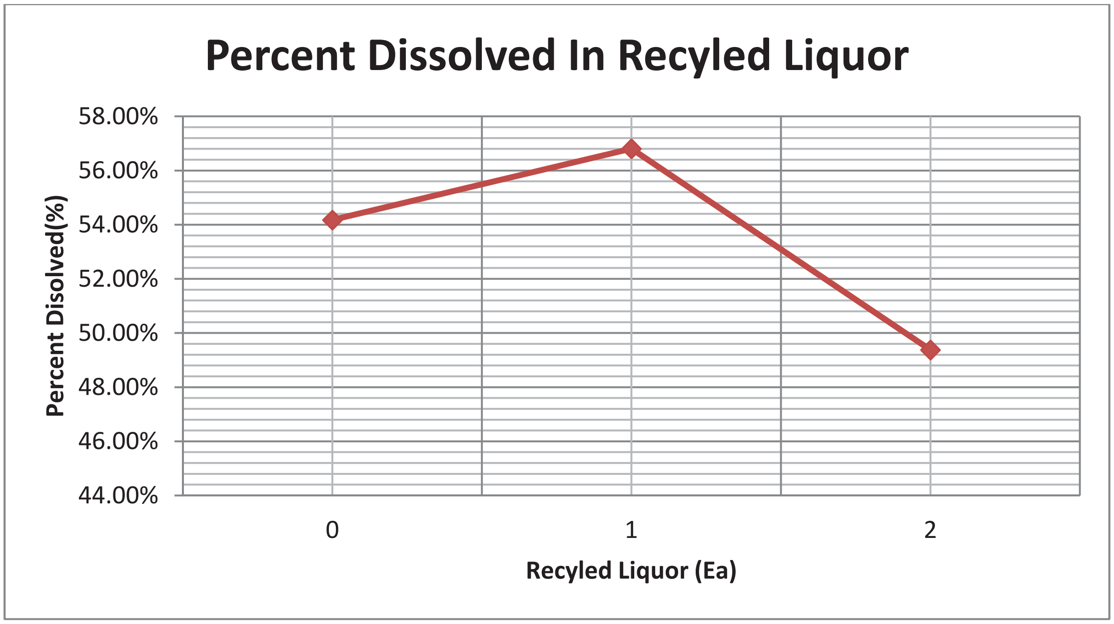

Figure 19. Sycamore lignocellulosic biomass extraction at 260°C 15 minute extraction and Recycled liquor.

4.8 Liquor Recycle and its Benefits to Butanol Production.

The recycling of the liquor with an increase in dissolved solids is significant. The recycling of the liquor makes it practical in an industrial setting.   Pulping paper mill process consists of steps that are similar to the process of producing butanol. The Kraft pulping process, other than the chemicals used in producing the pulp, is similar to the process used in the lab to obtain the required dissolved solids in the liquid. Figure 20 provides a schematic of the Kraft pulping process. 130 million tons/year of kraft pulp are produced globally, which is about two-thirds of the world's virgin pulp production (Tran, Honghi, tappi.org). There are approximately 426 closed paper mills in the United States (http://www.cpbis.gatech.edu/data/mills-online-new).

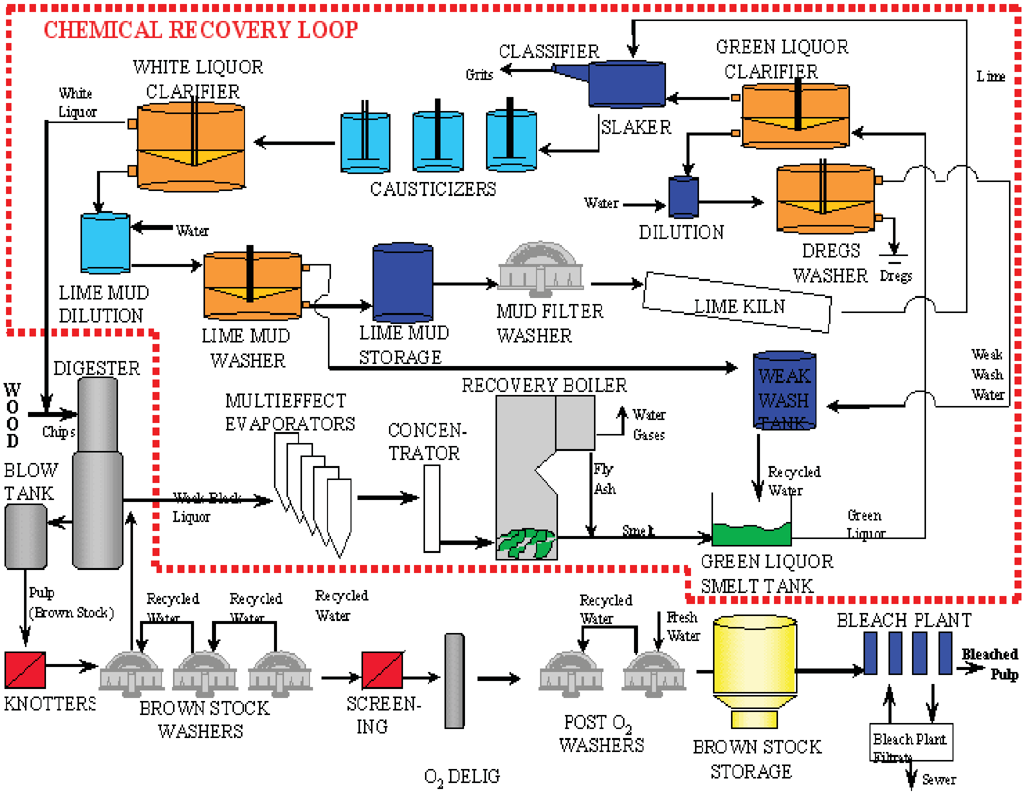

Figure 20. Kraft pulping process (http://cerig.efpg.inpg.fr/EFPG-days/2003/page63.htm)

The closed paper mills in the United States provide the infrastructure needed to produce butanol in the United States. Figure 21 provides a map of the United States with closed paper mills. There are three reasons to use closed paper mills in the United States the mechanical equipment already in place, the proximity of the plants to the raw materials needed for butanol production and the proximity of plants near markets for the distribution of the product.

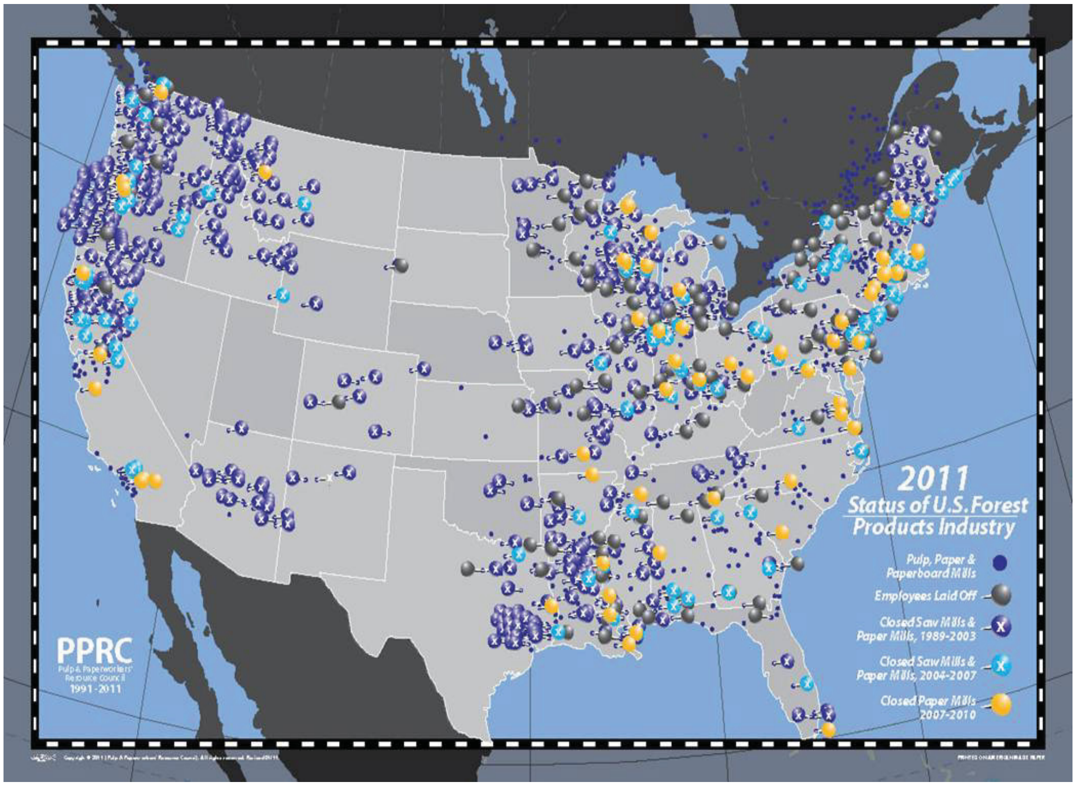

Figure 21. Status of U.S. Forest Products Industry (http: www. prc.info/html/millclosures.htm).

CHAPTER 5 - CONCLUSION

Research has shown that peak oil production is on the horizon where do we go from here? The population and the development of industrial nations are requiring the development of alternative fuels. The current fracking technology utilized for the massive recovery of natural gas should not curtail the development of alternative fuels. The development of alternative fuels is a necessity in the current global economy.

The use of cellulosic material such as wood in lieu of expensive feed stocks is the choice for alternative fuel production. Butanol production over ethanol is the future of alternative fuels due to the energy value and transportation in pipe lines. The cost of butanol versus gasoline at current market prices is very competitive.

The extraction of sugars from hardwoods by high temperatures and pressure has been proven to provide the ingredients for the fermentation process of butanol production. The research in this paper has showed that the maximum dissolved solids from hardwood feedstock can be obtained from a temperature of 250°C and a reaction time of sixty minutes. The research also showed that recycling of the liquor will produce an increase in dissolved solids.

The use of currently closed current paper mills in the United States could provide the infrastructure for the production of butanol due to the similar processes for extraction of solids dissolved from cellulosic materials such has hardwoods. The location of the mills near the existing lumber processing facilities will provide the raw material for the butanol production, and the locations of the closed paper mills throughout the United States will provide the required distribution sites.

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