

# **A Study Assessing the Opportunities and Potential of Corn-Based Products and Technologies**

Developed by:



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**Acronyms**

3-HPA – 3-Hydroxypropionic Acid  
ARS – Agricultural Research Service  
BBL – Barrel (of crude oil or other fuel)  
BDO – Butanediol  
BTU - British thermal units  
BTX – Benzene, Teluene and Xylene  
C5 – 5 carbon  
C6 – 6 carbon  
CDS – Condensed distillers solubles  
DDG – Dried distillers grains  
DDGS – Dried distillers grains with solubles  
DOE – Department of Energy  
GBL –  $\gamma$ -butyrolactone  
ME-THF – Methyl-Tetrahydrofuran  
Mmgy – Million gallons per year  
MSU – Michigan State University  
MBI – Michigan Biotechnology Institute  
NCERC – National Corn-to-Ethanol Center  
NREL – National Renewable Energy Laboratory  
ORNL – Oak Ridge National Laboratory  
PDO – 1,3- Propanediol  
PET – Polyethylene terephthalate  
PLA – Polylactic acid  
PNNL – Pacific Northwest National Laboratory  
PSI – Pounds per square inch  
PTT – Polytrimethylene terephthalate  
THF – Tetrahydrofuran  
USDA – United State Department of Agriculture  
WDG – Wet distillers grains  
WDGS – Wet distillers grain with solubles

### **Disclaimer**

This report was produced for the Agricultural Utilization Research Institute (“AURI”). Informa Economics, Inc. (“Informa”) has used the best and most accurate information available to complete this study. Informa is not in the business of soliciting or recommending specific investments. The reader of this report should consider the market risks inherent in any financial investment opportunity. Furthermore, while Informa has extended its best professional efforts in completing this analysis, the liability of Informa to the extent permitted by law, is limited to the professional fees received in connection with this project.

## I. Executive Summary

Based on demand/market potential, economic feasibility, stage of development and strength of institutional support, Informa Economics, Inc. (“Informa”) narrowed down a list of more than 100 emerging corn products and technologies to 8 of the most promising, considered to have the greatest potential to add significant value to Minnesota’s corn commodity production. However, as with the potential of any biobased product or technology, the development of these emerging corn products and technologies will be heavily reliant on future market price environments (especially for petroleum) and government policies. The following are what Informa considers to be the top 8 products and technologies for corn at this point in time, listed in alphabetical order.

### 1. Anaerobic Digestion

Anaerobic digestion uses bacteria to convert the thin or whole stillage by-product of ethanol production into biogas – a mixture of methane (50-80%), CO<sub>2</sub> (20-50%), and trace amounts of H<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>S, which can be burned for energy as a substitute for natural gas. This process reduces energy costs and greenhouse gas emissions and helps to conserve water relative to traditional corn-to-ethanol production. Furthermore, if collected, the struvite, a sludge that builds up in the digester, could be sold as a valuable fertilizer or a livestock feed additive.

It is estimated that anaerobic digestion using thin stillage can reduce the energy needs of an ethanol facility by 43-66%, and if using whole stillage, energy needs could be entirely met by the biogas. However, currently, it is not widely used by the ethanol industry at any significant scale, as current capital costs are significant.

### 2. Butanol

Butanol is currently produced mainly via petrochemical feedstocks and is used primarily as an industrial solvent. However, fermentation processes are currently being developed to produce “biobutanol”, and if cost competitive, it can also be used as a renewable fuel, greatly expanding its market potential. Butanol offers several key advantages over ethanol, including a higher energy content, the ability to transport it via pipeline, a lower reid vapor pressure which makes it safer to use and means that it generates fewer volatile organic compound emissions, and the ability to be blended with gasoline at higher levels. Additionally, several researchers are going one step further and are looking at ways to make higher valued products from butanol that can serve as gasoline, diesel and jet fuel replacements (not blends).

There have been many advancements made to the biobutanol production process over the last several decades and many of the challenges previously preventing butanol production from being economically viable have largely been resolved. The technology appears to be currently cost competitive with petrochemical based butanol (said to be economical at \$60/bbl crude oil) and also competitive or nearly competitive with ethanol. Of those companies currently pursuing its development,



the earliest stated year for expected commercial production is 2010, but many do not expect to see commercial scale production until 2011/2012.

### **3. Cellulosic Ethanol – Biochemical Platform**

Over the past few years, there has been significant research and development effort given toward improving the high production cost areas of biochemical cellulosic ethanol production: pretreatment, hydrolysis, and fermentation. There are essentially three key challenges involved in these processing steps. The first is the development of cost efficient pretreatments, which are necessary in order to open up the structure of the biomass sufficiently to allow for effective hydrolysis. Once the sugars are hydrolyzed, broken down into 5-carbon and 6-carbon sugars, they can then be fermented using biological agents (e.g., microorganisms, yeast) to produce ethanol. However, it is far more difficult, and thus more costly, to hydrolyze cellulosic biomass than it is to hydrolyze the starch from the traditional corn-to-ethanol process, and while hemicellulose is relatively easy to hydrolyze compared to cellulose (fractions of the lignocellulosic biomass), it is more difficult to ferment. Therein lie challenges two and three: hydrolyzing the cellulose and fermenting the xylose sugars released from the hemicellulose.

There are numerous companies and research institutions developing their own approaches and unique technologies to improve upon current pretreatment, hydrolysis and fermentation processes. However, the bottom line is that a cost efficient process has yet to be commercialized. There are several companies that are expecting to reach commercialization by 2011/2012. Yet, the tight capital market is inhibiting many from obtaining the capital needed to go forth with their commercialization efforts.

### **4. Ethanol Distillation**

Energy costs currently account for about 12% of overall operating costs of traditional corn-to-ethanol production, the second largest operating cost expenditure next to feedstock costs. Of the overall energy consumption, distillation and dehydration consume about 50% (McAloon et al., 2004; Kim and Dale, 2005 – cited by Vaperma). It is also one of the key cost components in the biochemical cellulosic ethanol platform. However, several alternative ethanol distillation technology developers claim to achieve a 40% reduction in energy costs over traditional distillation methods; this would equate to an approximate 6 ¢/gal cost savings, or \$3 million per year for a 50 million-gallon-per-year (mmgy) ethanol facility (using current natural gas prices). Additionally, according to one technology developer, Vaperma, overall fuel production could also be increased by 20% using their process.

Traditionally, the separation of ethanol and water is performed through a combination of steam distillation and a molecular sieve. However, there are various processes being developed whereby ethanol is removed during fermentation, reducing product inhibition and energy costs, and thereby also reducing greenhouse gas emissions. Alternative ethanol distillation technologies currently being developed include: vacuum stripping, gas stripping, membrane separation, solvent (liquid)

extraction, and supercritical CO<sub>2</sub>. While each of these methods has its own pros and cons, the leading technology at this time appears to be membrane separation. This technology uses membranes, which are vapor phase separation units, to allow the preferred permeation of water over other vapor components in a gas mixture. The removed ethanol is then distilled and the remaining fermentation broth is recycled.

These technologies are largely in the late development/early commercialization stage, and are expected to reach commercial status within 3-5 years, if not sooner.

## **5. Front-End Fractionation**

There are several front-end fractionation processes that separate the corn entering into the dry-mill ethanol facility into three fractions: pericarp (bran/fiber), germ (the oil-bearing portion of the kernel) and endosperm. Revenue streams generated from this process include corn oil; high protein, low fat and fiber distillers grains; fiber and ethanol. Additionally, according to some technology developer claims, front-end fractionation can reduce energy consumption and lower volatile organic compound emissions. Another benefit of fractionation comes in the form of risk mitigation, as producers are not relying solely on the revenues from two product markets and they have increased flexibility.

Front-end fractionation technologies can generally be classified as either wet fractionation processes or dry fractionation processes. In general, wet fractionation technologies tend to be more costly. However, they also produce higher-valued co-products and have less starch loss than dry fractionation technologies. In a new twist, the company MOR Technology claims to have developed a unique fractionation process known as MOR FRAC+ with costs similar to those generally associated with dry fractionation technologies but with the higher valued co-products and the lower starch loss generally associated with wet fractionation technologies. However, this technology is not yet proven at commercial scale.

## **6. 3-Hydroxypropionic Acid**

3-Hydroxypropionic acid (3-HPA) is a building block chemical that can be used to produce many other commodity and specialty chemicals used in a wide array of product applications including solvents, plastics and moldings, fibers and resins, composites, adhesives, coatings, aliphatic polyesters and copolyesters and disinfectants. One of the most promising aspects of this building block chemical is not only the current petrochemical products which it could potentially replace, but also the new and unique chemical properties it would bring to the market. Given its potential, it was identified by the U.S. Department of Energy (DOE) in 2004 as one of the top 12 chemicals from biomass sugars and syngas.

Cargill, along with Codexis and the Pacific Northwest National Laboratory, have already developed a bioprocess to produce 3-HPA which converts glucose or other carbohydrate sources into 3-HPA. 3-HPA can then be converted into a variety of high-value chemicals, including acrylic acid, 1,3-propanediol, malonic acid, and

acrylamide. In early 2008, Cargill announced a joint agreement with Novozymes to develop a technology enabling the production of the derivative acrylic acid. At the time of the announcement, the companies said they expected their technology to be ready in 5 years. However, through personal communication, Cargill has revealed that they no longer plan to pursue the development of 3-HPA, as they do not feel that the product has the ability to “bring profitability in a reasonable time.” This would indicate that this product/technology is more likely a long-term prospect, as the market potential still exists despite recent developments.

## **7. Succinic Acid**

Succinic acid is a building block chemical produced by converting the glucose and/or five carbon sugars from a variety of possible feedstocks, including corn, using a specific succinic acid fermenting microorganism and CO<sub>2</sub>. This building block chemical can be used to produce many other commodity and specialty chemicals used in a wide array of product applications, including solvents, coatings, adhesives, plastics, fibers, lubricating oils, diesel fuel oxygenates, personal care products and cosmetics. In addition to the many market applications for which succinic acid and its derivative chemicals can be applied, another promising attribute is that its production requires CO<sub>2</sub>, leading to what some claim to be a carbon negative process.

Its potential has been recognized by many countries and was identified by the DOE in 2004 as one of the top 12 chemicals from biomass sugars and syngas. Furthermore, this chemical can be used to produce other top 12 chemicals. If a technology is developed to produce biobased succinic acid that is cost competitive with similarly functioning petrochemicals, the potential world market is in excess of \$1 billion per year. And, according to one technology developer, Bioamber, commercial biobased succinic acid production is expected by 2011/2012.

## **8. Zein Extraction**

Various processes have been developed to extract zein protein from corn and corn by-products (e.g., distillers grains). Zein is a high-value protein which can be used in a wide range of applications. Zein is not used extensively in human food products, despite being edible, due to its negative nitrogen balance and poor water solubility. However, this insolubility is what makes zein and its resins form tough, glossy, hydrophobic grease proof coatings that are resistant to microorganisms, heat and humidity. Zein applications include: specialty coatings for pharmaceutical tablets, candies, nuts, and paper products, chewing gum, adhesives and binders, ink, cosmetics, fibers and textiles, resins and biodegradable plastics and high-value biomedical applications.

Currently, zein can be extracted from corn gluten meal, a by-product of the wet milling process. However, current extraction and purification technologies are such that the price of zein limits current market applications. Yet, there are several technology companies/institutions currently working to develop an economically viable extraction and/or purification process.

## **II. Introduction**

The Agricultural Utilization Research Institute (“AURI”) commissioned Informa Economics, Inc. (“Informa”) to assess and identify those existing and emerging products and technologies (both domestic and international) associated with the biobased economy that will boost economic opportunities for the corn and soybean agricultural sectors in the United States and the State of Minnesota. The overarching objective of the project was to specify eight products or technologies for each commodity which would likely add value to the corn and soybean complexes over the next ten years. This project has been achieved by conducting a blend of desk research (review of the literature) and targeted interviews, by phone and in-person, with the companies that are producing the biobased products and the scientists and technology leaders that are conducting ground-breaking research in the ever-evolving biobased economy. In the end, this study provides AURI with recommendations regarding which products and technologies show the most promise, thereby laying the foundation as a roadmap which will serve as valuable input to AURI in their strategic planning processes.

### **A. Report Layout**

This introductory section precedes two distinct reports that have been prepared for AURI. The two distinct reports are the analyses, findings and recommendations for the biobased products and technologies for the respective commodities of corn and soybeans. The “corn report” and “soybean report” are distinct and stand alone from each other. The role of this introductory section is to “set the stage” for each of the reports by discussing the project methodology and process flow and presenting a general overview of the biobased and energy economies. This overview should provide the reader a framework from which to better appreciate the opportunities and complexities of the technologies and products that are discussed in the corn and soybean reports.

### **B. Project Methodology and Process Flow**

The biobased economy is a rapidly changing environment where government policies combined with volatile commodity prices can dramatically affect the returns to the participants in said markets. Given this ever-changing context, it was important to provide solid fundamental research with both quantitative (when available) and qualitative analyses to ascertain the top promising corn and soybean products and technologies. It should be noted that the final so called “top eight winners” for each commodity should not be viewed as a list that is “set in stone” because of the uncertain nature of the markets surrounding energy and agricultural commodities. The products and technologies that have been identified as the top eight in both reports actually have the potential to move up or down in relative importance as policies change and technological breakthroughs occur over time. The study team took into consideration the issues of market and political uncertainty

when conducting the research. In the end, the goal was to provide recommendations to AURI regarding those products and technologies that have the highest probability of market success and can impact the State of Minnesota's economy.

The project could be characterized as being a continual flow process where feedback loops were put into place in order to test and retest the justification for including a product or technology in the study. Ultimately, the study was carried out in three Phases, which are summarized in Figure 1. The flow diagram highlights the use of multiple check points or "Phases" in order to "funnel" the products and technologies down to the two top eight lists. In Phase I, Informa conducted desk research that was extremely broad, identifying over 100 products and technologies each for corn and soybeans. Each product or technology was catalogued in a large matrix in which there was with a brief description of said product or technology, identification of the companies or institutions that are engaged in the respective "space," and also special notes.<sup>1</sup> In order to further refine the list in Phase I, four criteria were used by the research team in order to select a limited number of products and technologies that were deemed worthy for moving on to Phase II for more in-depth evaluation. The four criteria are based on those factors that are key characteristics for determining potential success in the marketplace. The four criteria were as follows:

### **1. Demand/Market Potential:**

This addresses the potential size (in value and volume) of the marketplace for a respective product or technology. Some biobased products or technologies, for example, may show significant promise regarding market penetration into existing markets or market adoption; however, the overall market may be extremely small and highly specialized. This means that the introduction of the product or technology would have very little impact to the economy at large. The economic returns or benefits would be confined to a very narrow sector of the economy because of the small market size. The ambition of the study team was to identify those products and technologies which are associated with bigger demand markets and thus potentially larger economic impacts.

### **2. Economic Feasibility:**

Just because a product can be produced or a technology can be used says nothing regarding the cost of producing the product or utilizing the technology. Some products or technologies have highly desirable results or characteristics; however, the cost associated with the product or technology is beyond what the marketplace will likely bear. It should be noted that economic feasibility can be accomplished by either public support (e.g., the 45 cent per gallon tax credit for ethanol production) or the ability of the product or technology to be produced in

<sup>1</sup> Note: Appendices at the end of each report display the large product and technology lists developed in Phase I.



such a manner that real economic returns are achieved without the aid of government support (or a blend of both the marketplace and government support as is the case for ethanol and biodiesel). The study team focused on specifying those products or technologies that would likely become commercially and economically viable over the next ten years.

### **3. Development Stage:**

The development stage is important in the context of the expected planning time horizon of AURI. AURI has established the objective for Informa to identify those products or technologies that will likely have a material economic impact over the next ten years. This means that some products or technologies that might have been identified as being very promising would not be considered for inclusion in the final list because they are too early in the development cycle. Many products or technologies display significant promise from a technical perspective, meaning the mechanical or chemical execution of said technology or product can be achieved in the laboratory or at the pilot scale of operation. Success at the pilot scale level is desirable; however, the more significant hurdle, is the ability to transfer the technology or product to a commercial scale such that they can be introduced into the marketplace and expected to compete with other more traditional products or technologies.

### **4. Strength of Institutional Support:**

The level of institutional support is critical for influencing the success or failure of launching a new product or technology. Institutional support can come in the form of either public or private support or a blend of both. Launching a new product on a “shoe string” budget out of someone’s garage is the exception rather than the rule regarding the probability of success. Those products or technologies which have deep funding sources and access to production and distribution infrastructure and systems generally have a higher likelihood of achieving market penetration and the necessary traction to remain economically viable in the long-run. Large corporations such as DuPont or Cargill are generally advantaged relative to much smaller capitalized companies regarding the ability to invest in the development of new products and technologies and bring them to market on a significant scale. U.S. Federal agencies such as the U.S. Department of Energy (DOE) have also played a vital role in the discovery process of new products and technologies. The DOE has spent billions of dollars helping to fund the discovery of new products and technologies playing the role of a basic research benefactor and even a venture capital firm, investing in emerging products and technologies where often the private sector has deemed the initiatives as being too early-stage or risky to fund completely on their own. The study team evaluated all of the products and technologies in light of the

perceived extent of public and private support for the respective product or technology.

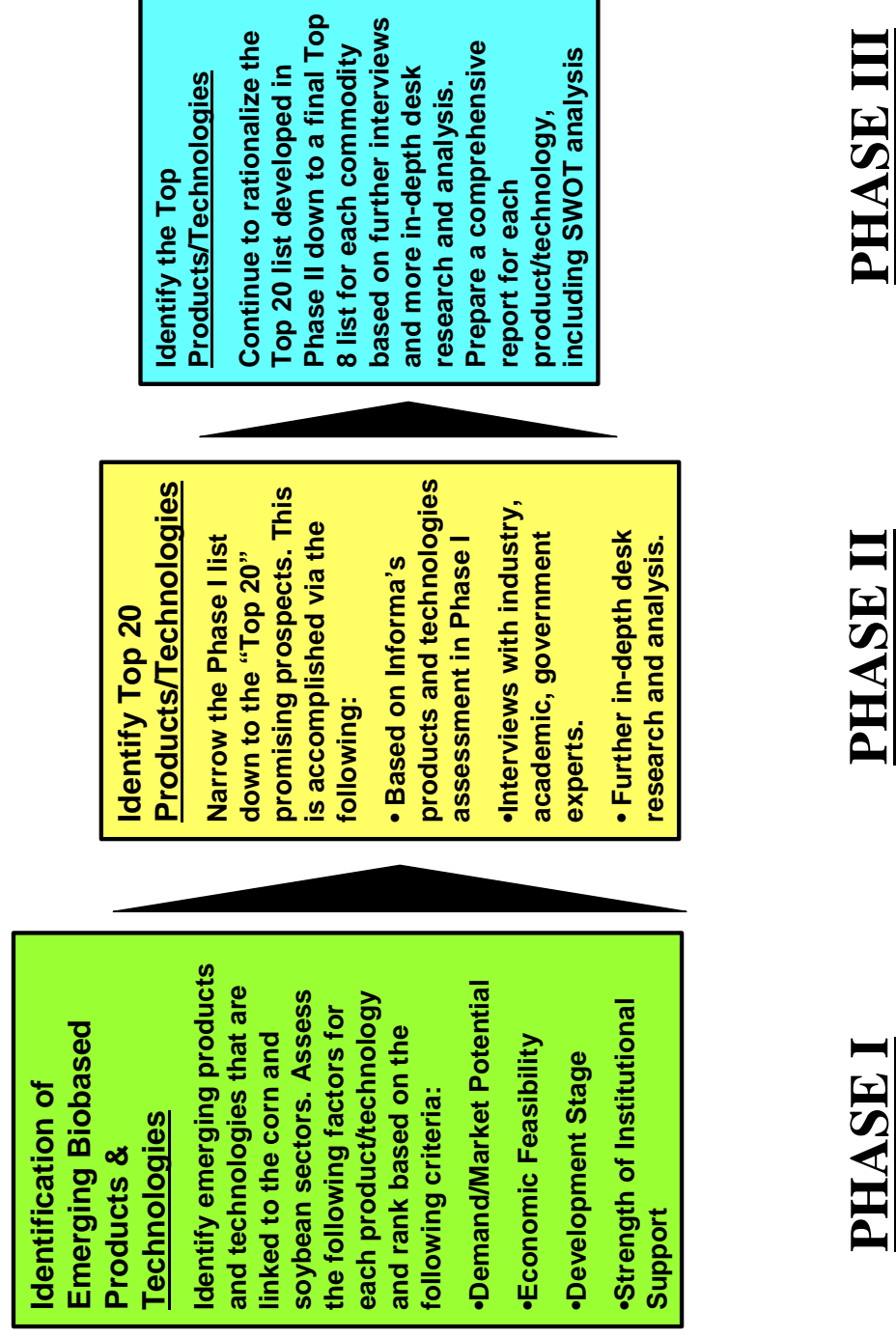
In Phase I quantitative scores were generated for each of the 100 products and technologies for corn and approximately 140 products and technologies for soybeans, where they were awarded a score of 10 (being the lowest), 20, 30 or 40 (being the highest) for each of the four criteria. Each of the four criteria was given different “weights” of importance, as follows: Demand/Market Potential 40%, Economic Feasibility 15%, Stage of Development 20% and Institutional Support 25%.<sup>2</sup> The combination of the criteria weights multiplied by the scores awarded each of the criteria generated a “weighted score” for each of the respective products or technologies. The Informa team independently scored and then ranked the products and technologies for corn and then soybeans. The scoring process was further refined to reflect an enhanced consensus of the team. The ranked scores led to a “Top 30” list for corn and a “Top 30 list” for soybeans. This concluded Phase I of the project.

Phase II began the process of refining the “Top 30” down to a “Top 20 list,” each for corn and soybeans. The study team then began to strategically engage a broad cross section of academic and industry experts with interviews (site visits and telephone interviews) in order to reduce the top 30 list down to top 20. Examples of interviews and trips are as follows: trip to the National Renewable Energy Laboratory (NREL), trip to the National Corn to Ethanol Research Center (NCERC), trip to the USDA Agricultural Research Service Laboratory in Peoria, IL, phone interviews with Oak Ridge National Laboratory, MBI International (Michigan Biotechnology Institute), and numerous other private sector researchers. The experts were asked to comment on the top 30 list to identify a number of key points, (1) specify if there were any omissions from the list, and if so, what products/technologies should be included, (2) identify what products or technologies should be removed from the list, (3) provide an opinion on what product/technologies should be included in the top 20, and (4) distinguish what their preferred top ten products/technologies were and explain in depth why. The Informa research team analyzed the findings from the interviews and constructed a product/technology top 20 list for each of the commodities.

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<sup>2</sup> It is acknowledged that the reader of this report might perceive the weights given to each of the criteria should be changed depending on their point of reference. Informa, however, spent a significant amount of time developing this quantitative framework in order to remain sensitive to AURI’s expectations and needs as an organization.

Figure 1: AURI Corn and Soybean Project Flowchart





The Informa research team then conducted more detailed desk research based on a consensus of the expert interviews and prepared brief position papers for each of the top 20 product/technologies for each commodity. The findings in Phase II formed the foundation for the final Phase III and the selection of the two “Top 8” lists. In Phase III highly targeted interviews were conducted for specific products/technologies. For example, succinic acid (a corn-based chemical) was a product that received significant attention and interest in the early stages of the project and was a logical product to move through Phase I and to Phase II and then into Phase III. Moving into Phase III, the team sought those individuals or firms that had special knowledge of succinic acid, such as MBI International and Bioamber (a firm that is dedicated to making succinic acid competitive with maleic anhydride). The highly targeted interviews and desk research in Phase III ultimately yielded the identification and selection of the “Top 8” products/technologies for corn and soybeans.

The selected top 8 products/technologies for corn and soybeans were then given detailed write-ups (more detailed than the top 20 write ups). Each of the detailed product/technology write ups includes an overview of the product/technology, an analysis of its market potential, profiles of the companies and research institutions that are involved in the space and SWOT analyses (Figure 2). SWOT analysis is a widely used and versatile paradigm for strategic planning where the acronym stands for Strengths, Weakness, Opportunities and Threats. The application of the SWOT model provided the framework to distill the key findings of research and analysis into a summary matrix which is easily understood and identifies the key aspects and issues for each products/technologies. Figure 2 displays the SWOT and how each product/technology was filtered through the grid structure. In the end, the key decision and policy makers at AURI have an authoritative reference tool to guide them in their strategic planning processes.

**Figure 2: SWOT Grid**

	Strengths	Weaknesses	Threats	Opportunities
Social				
Technology				
Economic				
Environment				
Political				

## **C. Energy Markets: A Foundation for Biobased Products and Technologies**

Petroleum is defined in Greek as being "rock oil" or more commonly known as crude oil. Crude oil or crude petroleum oil is a naturally occurring, flammable liquid found in rock formations in the Earth consisting of a complex mixture of hydrocarbons of various molecular weights, plus other organic compounds. Crude oil has always been a substance in plentiful supply; the demand for oil, however, has changed dramatically over time given the advent of the combustion engine and the rise of geopolitical tensions surrounding who owns the oil and where is the oil located. Initially, oil was not used as a fuel; in the 1860's oil was in fact hailed as a disinfectant, a vermin killer, hair oil, boot grease, and a cure for kidney stones. In 1933, the U.S. paid \$275,000 to Saudi Arabia's King Ibn Saud for an oil concession. The King actually thought he had sold the Americans sand, since the British did not think there was oil there. After five years of disappointment, the Americans struck oil in Saudi Arabia. One expert at the time described Saudi Arabia's oil as "the single greatest prize in all history," a prophetic statement for the ages.

The true importance of oil worldwide was not understood until World War I and especially, World War II. World War II brought to light the notion of national security and the importance of the U.S. government having a safe supply of oil. After World War II, and the beginning of widespread economic recovery, it became clear that the world was going to need a lot more oil than the companies of Socal and Texaco in Saudi Arabia could provide. Since World II, the global landscape of the supply and demand for oil has become even more complex as synchronistic global expansion of developing countries coupled with continued Middle East conflicts has placed a new premium on petroleum.

Interest in the area of biofuels and biobased products (based on renewable carbohydrate feedstocks such as corn) has increased dramatically over the last ten years as energy prices, primarily crude oil, reached record highs. As described in this section, consumption of crude oil and refined products is on a very large scale, and as a result the potential market for biofuels and certain biobased replacements for petrochemicals is large.

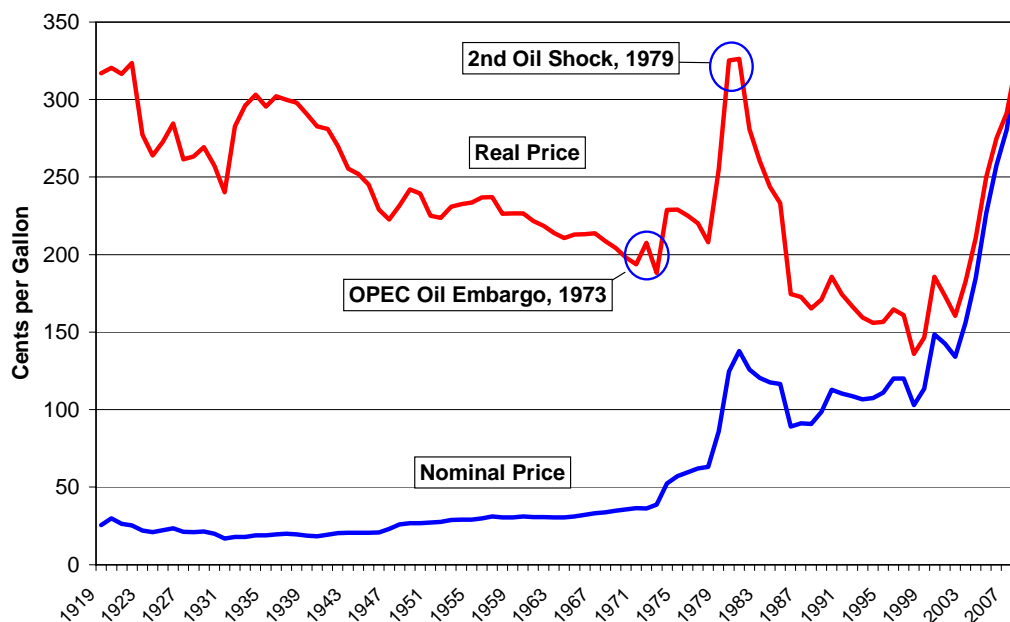
The recent price shock of 2008, quickly reminded U.S. consumers of their vulnerability and dependence on foreign sources of oil. Crude oil prices, as benchmarked by West Texas Intermediate (WTI) averaged only \$19.09/barrel from 1986 to 1999, ranging from a low of \$10.25/barrel to a high of \$41.07 during this period of time. As global economies rapidly expanded and the infrastructure to supply oil increased at a much slower pace, nominal oil prices for the WTI crude reached record high levels on July 3, 2008, at \$145.31/barrel (Figure 3). Adjusted for inflation, oil prices were actually in a long run decline since 1919 (Figure 4), with only brief price spikes. The 2008 jump in oil prices, however, elevated real prices to levels not experienced since the oil shock experienced in the late 1970's and early 1980's.

**Figure 3: Crude Oil Price, West Texas Intermediate: January 02, 1986 to June 16, 2009 (daily prices, nominal dollars)**



Source: U.S. Department of Energy, Energy Information Administration and Informa Economics.

**Figure 4: U.S. Real Gasoline Pump Price: Annual Average 1919-2008 (consumers price index-urban, 1982-84=1.00)**

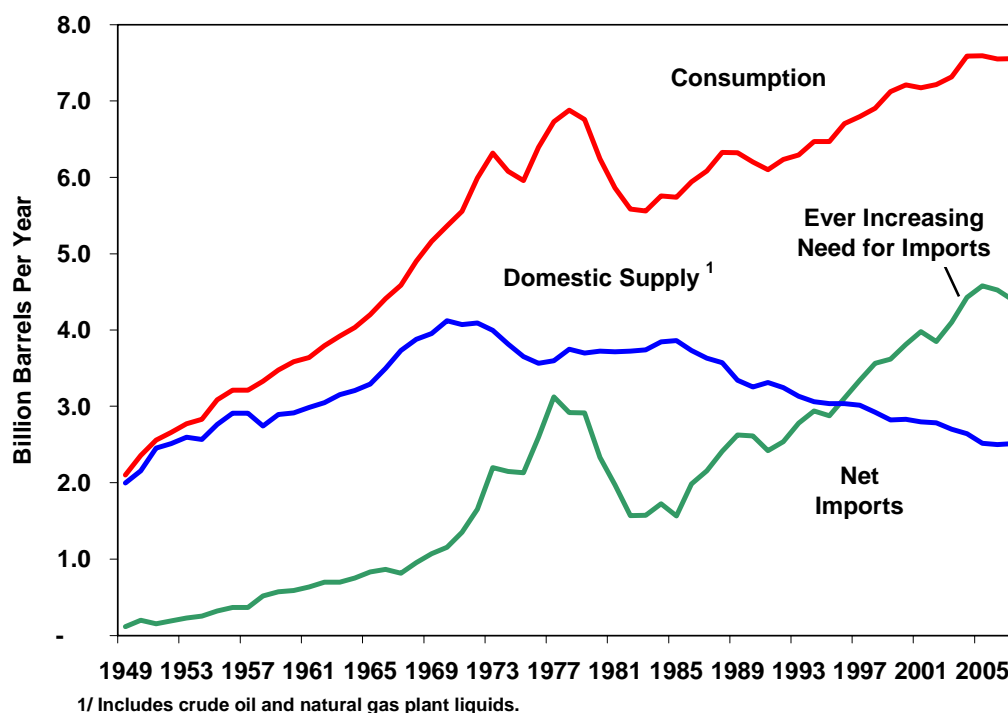


Source: U.S. Department of Energy, Energy Information Administration.

The higher real petroleum prices, concern over a slowdown in the development of new supplies of oil and the September 11, 2001, terrorist attacks and subsequent wars in Afghanistan and Iraq have renewed an interest of the American public in finding ways to reduce this country's dependence on foreign imports of petroleum and develop new technologies that consume less gasoline, such as the upcoming Chevy Volt, with claims of achieving 230 miles per gallon (mpg.). In 2006, the Bush administration acknowledged the need to find alternative, and preferably renewable, sources of energy. President Bush outlined in his 2006 State of the Union Address, the announcement of The Advanced Energy Initiative, which is designed to "help break America's dependence on foreign sources of energy." Former President Bush set as a national goal the replacement of more than 75% of the oil imports from the Middle East by 2025. The Advanced Energy Initiative provided for a 22% increase in clean-energy research at the U.S. Department of Energy. The intent of the funding increase was to accelerate breakthroughs in two critical areas, how we power our homes and businesses, and how we power our automobiles, thus stimulating a reduction in our country's demand for fossil based energy sources. The new Obama administration has followed through with a clear mandate to continue the country's need to address the energy predicament with new solutions. President Obama's comprehensive energy plan calls for some of the following initiatives:

- Help create five million new "green" jobs by strategically investing \$150 billion over the next ten years to catalyze private efforts to build a clean energy future.
- Within 10 years save more oil than we currently import from the Middle East and Venezuela combined.
- Put 1 million plug-in hybrid cars (cars that can get up to 150 miles per gallon) on the road by 2015; cars that will be built in America.
- Ensure 10% of our electricity comes from renewable sources by 2012, and 25% by 2025.
- Implement an economy wide cap and trade program to reduce greenhouse gas emissions 80% by 2050.

Statistics are very clear and impartial regarding the trends of oil consumption and production in the U.S. Since the mid-1950s, the U.S. has imported more energy than it has exported. Consumption of petroleum, the most prominent U.S. energy resource, has expanded from 6.2 million barrels/day in 1950 to almost 20 million barrels/day in 2007, or an annual total of 7.5 billion barrels (Figure 5). During this period, petroleum imports have grown from being insignificant to surpassing U.S. domestic supplies. Most oil imports have been met by North American countries, with Canada and Mexico providing over 29.2% of U.S. petroleum needs in 2008 (Table 1). The U.S. is faced with the continual concern of consistent supplies in the future from politically sensitive regions such as the Middle East. In 2008, OPEC countries accounted for over 46% of U.S. oil imports. Saudi Arabia represented 11.9%, Venezuela 9.2% and Nigeria 7.7% of total U.S. oil imports in 2008.

**Figure 5: US Petroleum Situation: 1949-2007**

Source: U.S. Department of Energy, Energy Information Administration.

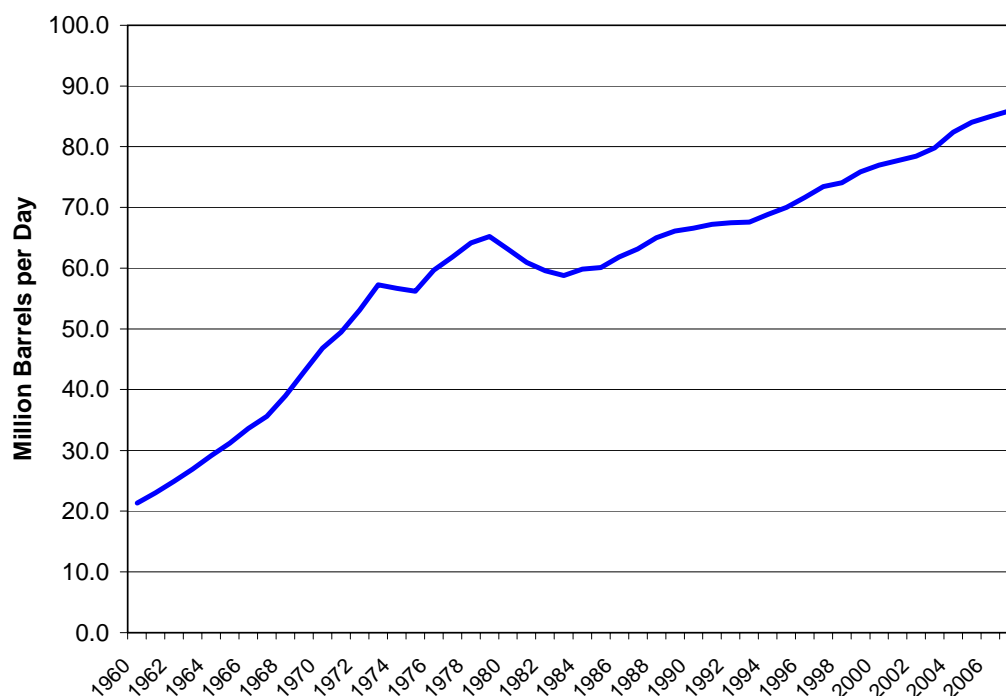
**Table 1: U.S. Imports of Crude Oil, by Country of Origin for 2008**

	Country of Origin	Thousand Barrels	Percent Total
1	Canada	899,935	19.1%
2	Saudi Arabia	560,705	11.9%
3	Mexico	475,545	10.1%
4	Venezuela	435,769	9.2%
5	Nigeria	362,263	7.7%
6	Iraq	229,300	4.9%
7	Algeria	200,192	4.2%
8	Angola	187,761	4.0%
9	Russia	169,415	3.6%
10	Virgin Islands (U.S.)	117,191	2.5%
	Rest of World		22.8%
<b>Total</b>		<b>4,711,238</b>	<b>100.0%</b>
<b>Non OPEC Countries</b>		<b>2,530,488</b>	<b>53.7%</b>
<b>Persian Gulf</b>		<b>868,516</b>	<b>18.4%</b>
<b>Total OPEC Countries</b>		<b>2,180,750</b>	<b>46.3%</b>

Source: U.S. Department of Energy, Energy Information Administration.

The global supply of and demand for energy is being challenged not just by the level of U.S. consumption and political instability in certain oil-producing countries, but also by growing demand in emerging economies such as China and India. World consumption of petroleum rose from just over 20 million barrels/day in 1960 to 85.9 million barrels/day in 2007, a compound annual growth rate of 3.12% (Figure 6).

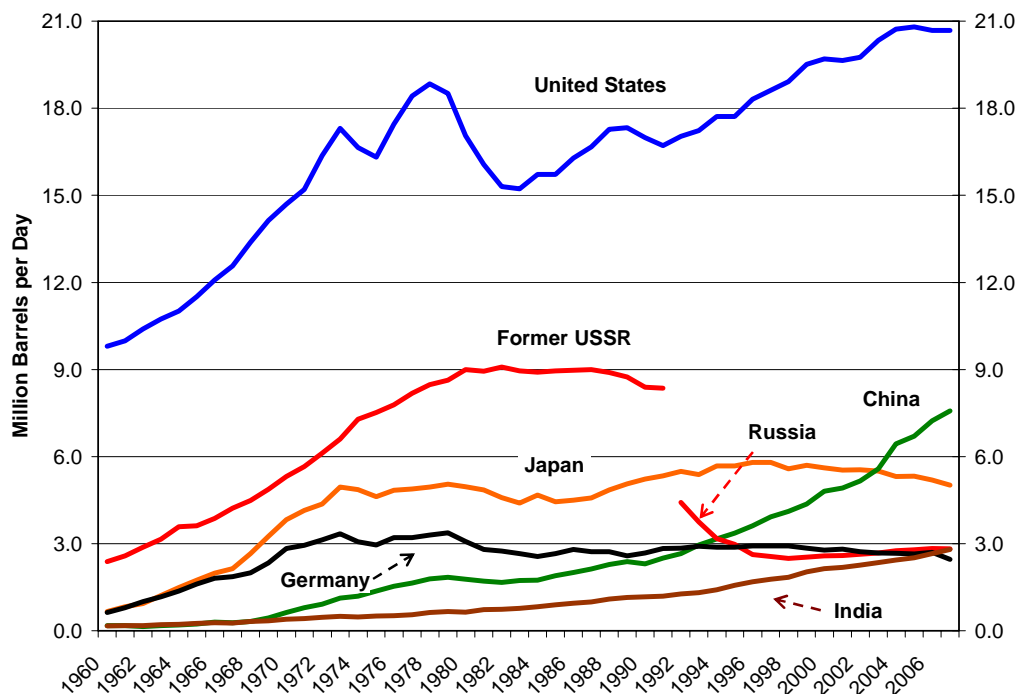
**Figure 6: World Daily Consumption of Petroleum, 1960-2007**



Source: U.S. Department of Energy, Energy Information Administration.

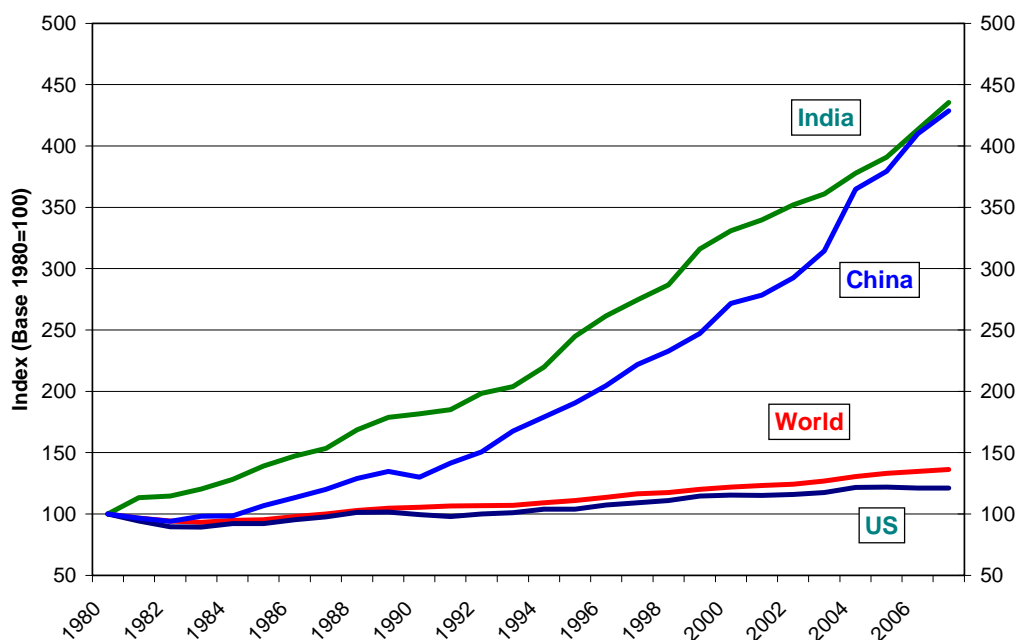
The U.S. is the most significant petroleum-consuming economy in the world (Figure 7). The former Soviet Union was second in importance until its breakup in the early 1990s; now China is the second-largest petroleum consuming economy. Since 1960, China has increased its consumption of petroleum faster than any country (over 3,000%), while India has increased consumption by almost 1,500% (Figure 8). More mature economies such as the U.S. and Canada actually exhibit growth rates that are below the world trend, this is also true for most of the major and mature economies in the European Union.

**Figure 7: Leading Petroleum Consuming Countries, Average Daily Consumption, 1960-2007**



Source: U.S. Department of Energy, Energy Information Administration and Informa Economics.

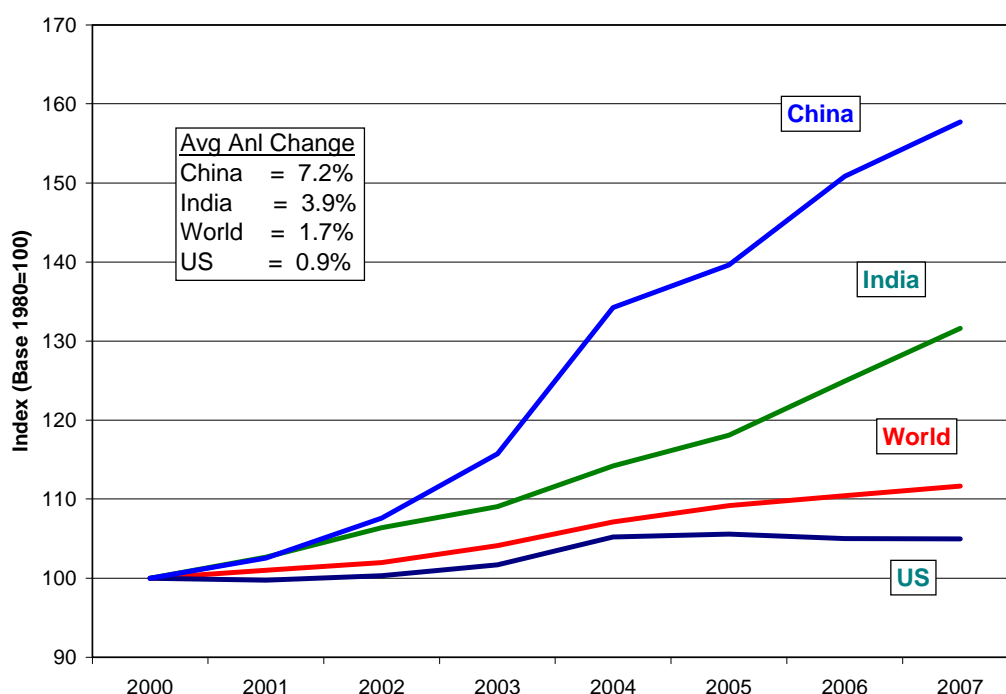
**Figure 8: Indexed Growth of Petroleum Consumption for Key Countries, 1980-2007 (Barrels of Oil Consumed Daily)**



Source: U.S. Department of Energy, Energy Information Administration and Informa Economics.

In recent years, the rate of growth for China, for example, has increased significantly (Figure 9). From 2000 to 2007, China's consumption of oil increased at an average annual rate of 7.2%; this was almost twice as fast as India's annual growth rate and significantly ahead of the U.S. annual growth rate of only 0.9%.

**Figure 9: Indexed Growth of Petroleum Consumption for Key Countries, 2000-2007 (barrels of oil consumed daily)**



Source: U.S. Department of Energy, Energy Information Administration and Informa Economics.

As previously mentioned, many European Union countries have generally fallen in their level of consumption of petroleum globally as emerging economies have rapidly increased their share of total petroleum demand (Table 2). From 1960 to 1969, the U.S. consumed, on average, 37.6% of the total global use of petroleum; the next largest oil consumer was the Former Soviet Union (FSU) at 11.6% (Table 3). Now the FSU has been dissolved and numerous developing countries have significantly expanded their economies, while the U.S. share of global oil consumption has actually declined to 25.7%, still extremely large; however, the impact of growing foreign economies is palpable. For example, often overshadowed by China and India, Brazil has also experienced rapid consumption in petroleum over the last 20 years (Table 4). Spain and Russia have also exhibited strong recent relative growth in oil consumption from 2000 to 2008.



**Table 2: Petroleum Consumption, Daily Average Barrels Consumed, Key Countries, 1960-2008 (million barrels)**

	1960-69	Rank	1970-79	Rank	1980-89	Rank	1990-99	Rank	2000-08	Rank
<b>WORLD</b>	<b>30.74</b>		<b>57.03</b>		<b>61.84</b>		<b>70.26</b>		<b>81.62</b>	
<b>Total OECD</b>	<b>22.47</b>		<b>40.41</b>		<b>39.11</b>		<b>44.66</b>		<b>48.65</b>	
<b>Total Non-OECD</b>	<b>8.27</b>		<b>16.62</b>		<b>22.72</b>		<b>25.60</b>		<b>32.97</b>	
<b>United States</b>	11.56	(1)	16.98	(1)	16.27	(1)	17.878	(1)	20.17	(1)
<b>China</b>	0.24	(12)	1.28	(9)	1.93	(5)	3.294	(3)	6.25	(2)
<b>Japan</b>	1.69	(3)	4.65	(3)	4.69	(3)	5.564	(2)	5.26	(3)
<b>Russia</b>							3.068	(4)	2.73	(4)
<b>Germany</b>	1.45	(4)	3.13	(4)	2.73	(4)	2.862	(5)	2.67	(5)
<b>India</b>	0.24	(13)	0.51	(13)	0.88	(13)	1.524	(13)	2.47	(6)
<b>Brazil</b>	0.36	(9)	0.86	(10)	1.15	(11)	1.767	(12)	2.23	(7)
<b>Canada</b>	1.10	(6)	1.76	(8)	1.63	(9)	1.829	(9)	2.21	(8)
<b>South Korea</b>	0.05	(14)	0.33	(14)	0.61	(14)	1.772	(11)	2.17	(9)
<b>Mexico</b>	0.35	(10)	0.75	(12)	1.48	(10)	1.858	(8)	2.04	(10)
<b>France</b>	1.05	(7)	2.33	(5)	1.87	(6)	1.935	(6)	2.00	(11)
<b>Italy</b>	0.97	(8)	1.93	(7)	1.80	(7)	1.900	(7)	1.78	(12)
<b>United Kingdom</b>	1.42	(5)	2.07	(6)	1.66	(8)	1.810	(10)	1.76	(13)
<b>Spain</b>	0.25	(11)	0.83	(11)	0.94	(12)	1.177	(14)	1.55	(14)
<b>Former USSR</b>	3.56	(2)	7.16	(2)	8.94	(2)				

Source: U.S. Department of Energy, Energy Information Administration, and Informa Economics.

**Table 3: Percent Share of World Petroleum Consumed by Key Countries, 1960-2008**

	1960-69	Rank	1970-79	Rank	1980-89	Rank	1990-04	Rank	2000-08	Rank
<b>WORLD</b>	<b>100%</b>		<b>100%</b>		<b>100%</b>		<b>100%</b>		<b>100%</b>	
<b>Total OECD</b>	<b>73.1%</b>		<b>70.9%</b>		<b>63.3%</b>		<b>63.6%</b>		<b>59.6%</b>	
<b>Total Non-OECD</b>	<b>26.9%</b>		<b>29.1%</b>		<b>36.7%</b>		<b>36.4%</b>		<b>40.4%</b>	
<b>United States</b>	37.6%	(1)	29.8%	(1)	26.3%	(1)	25.4%	(1)	24.7%	(1)
<b>China</b>	0.8%	(12)	2.2%	(9)	3.1%	(5)	4.7%	(3)	7.7%	(2)
<b>Japan</b>	5.5%	(3)	8.1%	(3)	7.6%	(3)	7.9%	(2)	6.4%	(3)
<b>Russia</b>							4.4%	(4)	3.3%	(4)
<b>Germany</b>	4.7%	(4)	5.5%	(4)	4.4%	(4)	4.1%	(5)	3.3%	(5)
<b>France</b>	0.8%	(7)	0.9%	(5)	1.4%	(6)	2.2%	(6)	3.0%	(6)
<b>Canada</b>	1.2%	(6)	1.5%	(8)	1.9%	(9)	2.5%	(7)	2.7%	(7)
<b>South Korea</b>	3.6%	(14)	3.1%	(14)	2.6%	(14)	2.6%	(8)	2.7%	(8)
<b>Mexico</b>	0.2%	(10)	0.6%	(12)	1.0%	(10)	2.5%	(9)	2.7%	(9)
<b>Brazil</b>	1.1%	(9)	1.3%	(10)	2.4%	(11)	2.6%	(10)	2.5%	(10)
<b>Italy</b>	3.4%	(8)	4.1%	(7)	3.0%	(7)	2.8%	(11)	2.4%	(11)
<b>United Kingdom</b>	3.1%	(5)	3.4%	(6)	2.9%	(8)	2.7%	(12)	2.2%	(12)
<b>India</b>	4.6%	(13)	3.6%	(13)	2.7%	(13)	2.6%	(13)	2.2%	(13)
<b>Spain</b>	0.8%	(11)	1.5%	(11)	1.5%	(12)	1.7%	(14)	1.9%	(14)
<b>Former USSR</b>	11.6%	(2)	12.5%	(2)	14.5%	(2)				

Source: U.S. Department of Energy, Energy Information Administration, and Informa Economics.

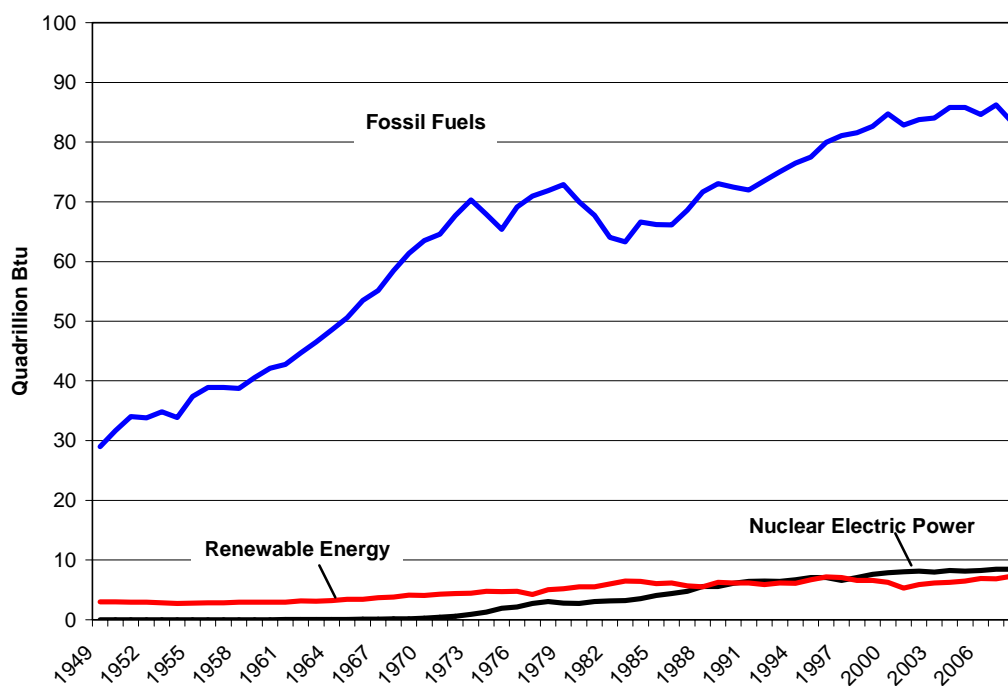
**Table 4: Annual Growth Rate of Petroleum Consumption in Key Countries, 1960-2008**

	Anl Rate 1960-69		Anl Rate 1970-79		Anl Rate 1980-89		Anl Rate 1990-99		Anl Rate 2000-08	
		Rank		Rank		Rank		Rank		Rank
<b>WORLD</b>	7.5%		3.4%		0.8%		1.5%		1.5%	
<b>Total OECD</b>	7.6%		2.4%		0.3%		1.6%		0.2%	
<b>Total Non-OECD</b>	7.4%		5.9%		1.7%		1.3%		3.5%	
<b>China</b>	11.4%	(7)	10.9%	(1)	4.0%	(3)	7.0%	(1)	6.8%	(1)
<b>India</b>	8.3%	(8)	5.1%	(7)	6.2%	(1)	6.4%	(3)	4.1%	(2)
<b>Brazil</b>	6.1%	(11)	8.5%	(4)	2.5%	(5)	4.8%	(4)	1.8%	(3)
<b>Canada</b>	6.0%	(12)	2.6%	(8)	-0.5%	(12)	2.0%	(6)	1.7%	(4)
<b>Russia</b>							-8.4%	(14)	1.5%	(5)
<b>Spain</b>	18.6%	(2)	6.0%	(5)	-0.5%	(11)	3.6%	(5)	1.2%	(6)
<b>Mexico</b>	4.9%	(13)	8.6%	(3)	2.7%	(4)	0.8%	(10)	1.0%	(7)
<b>South Korea</b>	26.1%	(1)	10.8%	(2)	4.9%	(2)	6.5%	(2)	0.4%	(8)
<b>United States</b>	4.1%	(14)	2.5%	(9)	0.8%	(6)	1.7%	(7)	0.4%	(9)
<b>United Kingdom</b>	7.9%	(9)	-1.8%	(14)	0.3%	(7)	0.0%	(13)	0.0%	(10)
<b>France</b>	11.5%	(6)	1.5%	(11)	-2.0%	(14)	0.9%	(9)	-0.3%	(11)
<b>Germany</b>	12.6%	(5)	1.4%	(12)	-1.0%	(13)	0.5%	(11)	-1.2%	(12)
<b>Italy</b>	13.1%	(4)	1.0%	(13)	-0.1%	(9)	0.4%	(12)	-1.6%	(13)
<b>Japan</b>	16.1%	(3)	2.4%	(10)	0.1%	(8)	1.0%	(8)	-1.7%	(14)
<b>Former USSR</b>	7.6%	(10)	5.4%	(6)	-0.2%	(10)				

Source: U.S. Department of Energy, Energy Information Administration, and Informa Economics.

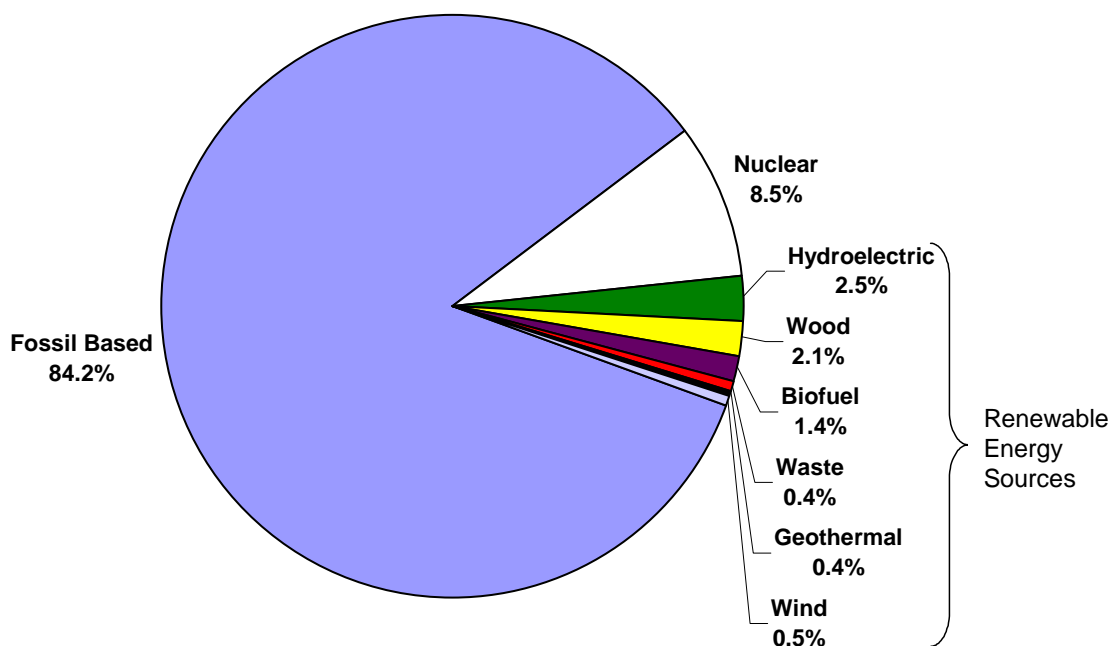
Since 1949, fossil fuel as a percentage of total U.S. energy consumption has risen considerably relative to nuclear electric power and renewable energy sources (Figure 10). The U.S. consumed almost 30 quadrillion Btu of fossil fuels in 1949; this has increased significantly to approximately 85 quadrillion Btu of fossil fuels in 2008. Just as the U.S. relies heavily on petroleum as a primary source of energy, other sources play a significant role in the intricate energy balance (Figure 11). The U.S. uses an extensive amount of natural gas, coal, and nuclear electric power, with renewable energy growing more popular. In 2008, fossil fuel-based energy sources (coal, natural gas and petroleum) accounted for 84.2% of total U.S. energy consumed, with the remainder being nuclear electric power (8.5%) and renewable energy (7.3%).

**Figure 10: Energy Consumption by Source, 1949-2008**



Source: U.S. Department of Energy, Energy Information Administration

**Figure 11: Percent Energy Consumption by Source, 2008**

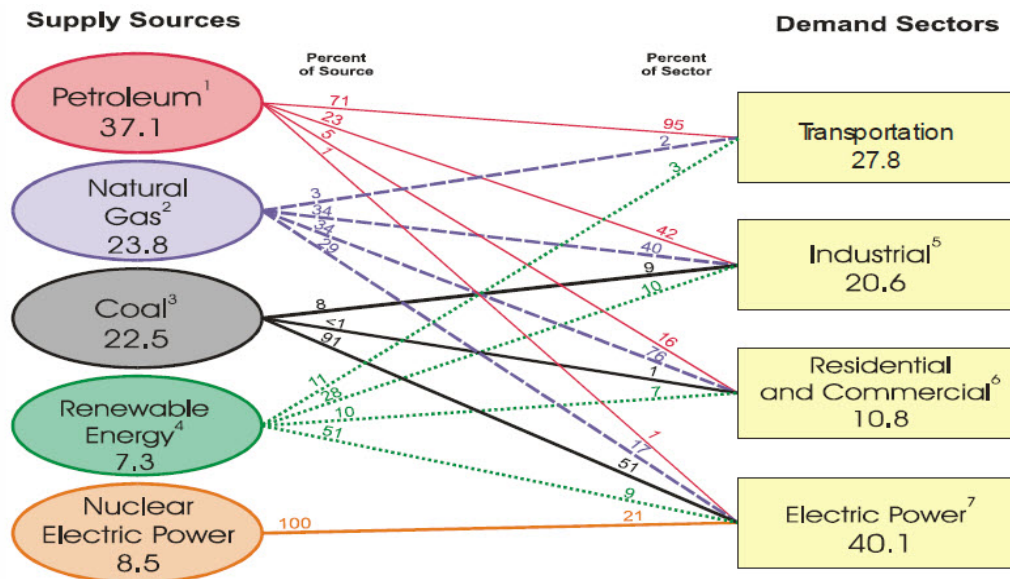


Source: U.S. Department of Energy, Energy Information Administration

There are four primary energy consuming sectors in the U.S. The four sectors are: residential, which accounts for 21.9% of the total energy consumption; commercial, which accounts for 17.9% of the total energy consumption; industrial, which accounts for 32.1% of the total energy consumption; and transportation, which accounts for 28.1% of the total energy consumption (Figure 12). Highlights of the supply/demand balance flow diagram are as follows:

- Transportation uses the largest share of petroleum at 71%, while the industrial sector uses 23% of petroleum and the remaining 6% goes to residential/commercial and electric power.
- The consumption of natural gas is evenly distributed between three sectors, with industry using 34%, residential/commercial using 34% and electric power using 29%; the remainder is consumed by transportation at only 3%.
- The consumption of coal primarily linked to two sectors, the generation of electricity at 91% and industrial consumption at 8%.
- Nuclear electric power is used exclusively, at 100% consumption, by the electric power demand sector.
- The use of renewable energy is divided across all four demand sectors with electric power using the most at 51% and industrial demand the second largest sector using 28%.

**Figure 12: U.S. Primary Energy Consumption by Source and Sector, 2007 (Quadrillion Btu)**



Source: USDOE, Energy Information Administration, Annual Energy Review 2007.

- 1 Excludes 0.6 quadrillion Btu of ethanol, which is included in "Renewable Energy."
- 2 Excludes supplemental gaseous fuels.
- 3 Includes 0.1 quadrillion Btu of coal coke net imports.
- 4 Conventional hydroelectric power, geothermal, solar/PV, wind, and biomass.
- 5 Includes industrial combined-heat-and-power (CHP) and industrial electricity-only plants.
- 6 Includes commercial combined-heat-and-power (CHP) and commercial electricity-only plants.
- 7 Electricity-only and combined-heat-and-power (CHP) plants whose primary business is to sell electricity, or electricity and heat, to the public.

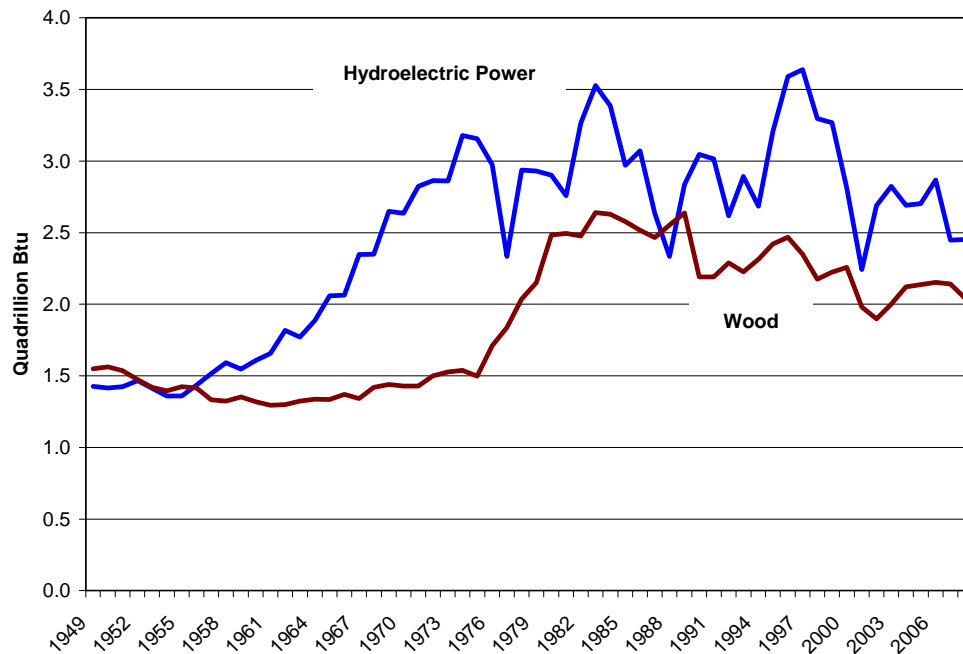
Briefly, the renewable energy sources can be segmented into the following general categories:

- Hydroelectric: Renewable energy from hydroelectricity.
- Wood: Wood, black liquor, and other wood waste.
- Waste: Municipal solid waste, landfill gas, sludge waste, tires, and agricultural byproducts, including animal waste, and other biomass (plant material and residue)
- Biofuels: Ethanol blended into motor gasoline and biodiesel.

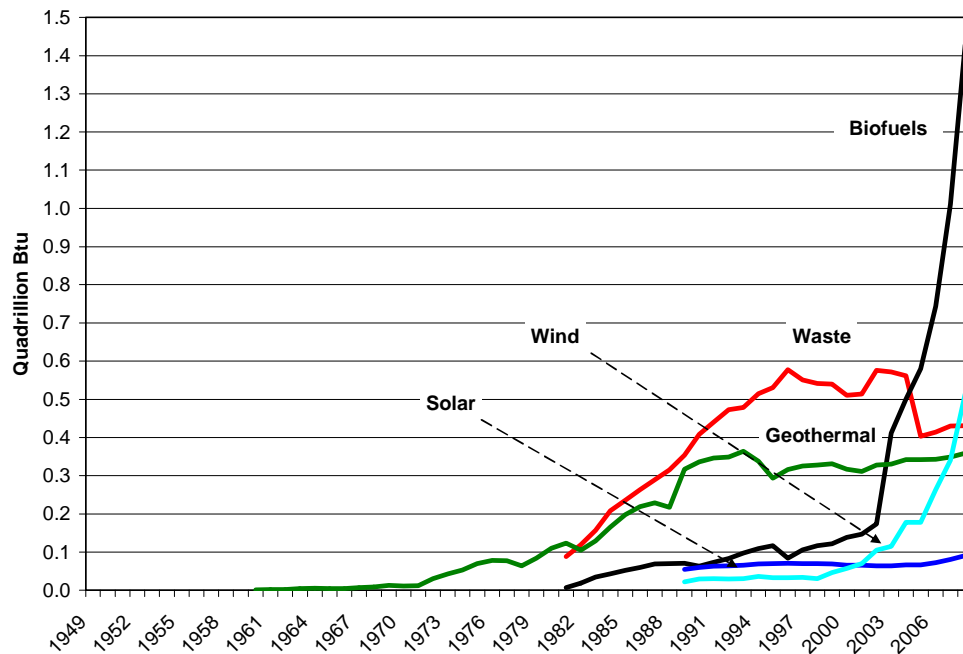
- Geothermal: Geothermal electricity net generation, heat pump, and direct use energy.
- Solar: Solar thermal and photovoltaic electricity net generation, and solar thermal direct use energy.

Hydroelectric power and wood-based power contribute the largest amount of renewable energy by a wide margin (Figure 13). However, their growth has remained flat since the 1980s. In general, other renewable energy sources have shown greater increases in their rate of adoption. Alcohol (ethanol) and wind based renewables have grown the most significantly from 1990 to the present (Figure 14).

**Figure 13: U.S. Renewable Energy Consumption by Source - Part I, 1949-2008**

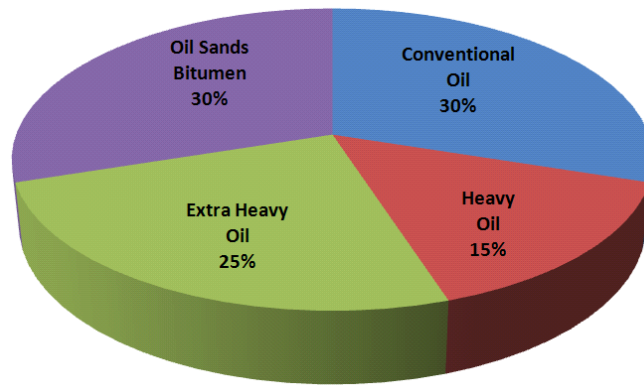


Source: U.S. Department of Energy, Energy Information Administration, Monthly Energy Review.

**Figure 14: U.S. Renewable Energy Consumption by Source - Part II, 1949-2008**

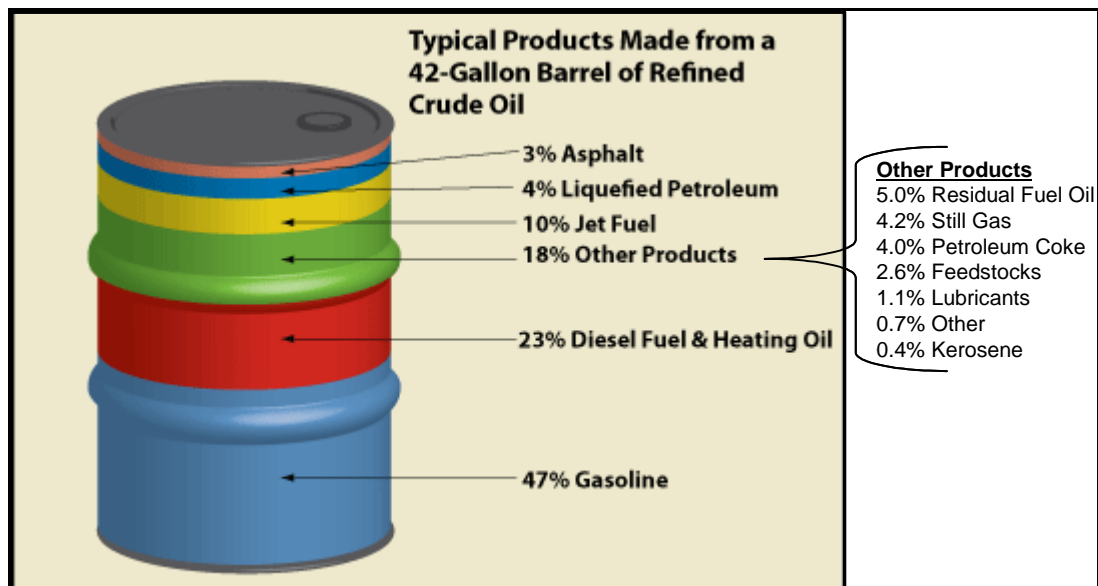
Source: U.S. Department of Energy, Energy Information Administration, Monthly Energy Review.

Today's marketplace is making a concerted effort to find larger supplies of renewable energy feedstocks and substitutes in order to replace the traditional fossil fuel (hydrocarbon based) sources of energy, as evidenced by such strong growth in the biofuels and wind sectors. Global economies are concerned that the supplies of conventional oil are declining rapidly and that the supplies of conventional oil might have passed what is called "peak oil." Peak oil is defined as the point in time when the maximum rate of global petroleum extraction is reached, after which the rate of production enters terminal decline. The concept is based on the observed production rates of individual oil wells, and the combined production rate of a field of related oil wells. The aggregate production rate from an oil field over time usually grows exponentially until the rate peaks and then declines, sometimes rapidly, until the field is depleted. Given the recent record prices for crude oil, the peak oil debate has gained significant attention with strong arguments both for and against the concept. Some experts have now estimated that total world reserves of *conventional* oil are now less than 30% of total oil supplies which include heavy oil, oil sands and extra heavy oil (Figure 15). The heavier oils are not easy to use (require special refining procedures) and are more expensive to extract compared to conventional oil. In addition to concerns over peak oil, energy security and mitigation of climate change are important reasons for the move toward biofuels and wind energy.

**Figure 15: Total World Oil Reserves**

Source: Alboudwarej, Husswin, Highlighting Heavy Oil, Oilfield Review, Summer 2006.

One of the reasons that conventional oil has become such a vital link and input in global economies is because of its chemical versatility which provides a plethora of uses. When refined, one barrel of crude oil yields about 19 gallons of finished motor gasoline, 9 gallons of diesel fuel, as well as other petroleum based derivatives used in products such as ink, crayons, bubble gum, dishwashing liquids, deodorant, eyeglasses, records, tires, ammonia, and heart valves, etc. (Figure 16).

**Figure 16: Products Made from a Barrel of Crude Oil<sup>3</sup>**

Source: USDOE, Energy Information Administration and American Petroleum Institute.

<sup>3</sup> Note: Percentages total 105% because of “processing gain.” A 42 gallon barrel of oil actually yields 44 gallons of products.



In general, each barrel of oil in the U.S. is fractionated into fairly consistent components as described below.<sup>4</sup>

- **Gasoline:** Of all the crude oil refined for use in the United States, almost half (47%) becomes gasoline for automobiles, boats and other gasoline-driven motors.
- **Jet Fuel:** Airplanes utilize approximately 10% of a refined barrel of oil in the form of jet fuel.
- **Diesel Fuel and Home Heating Oil:** 23% becomes distillate, two-thirds of which is refined for diesel fuel for trucks, buses and other diesel engines, while the remaining one-third is used as home heating oil.
- **Boiler Oil:** Boiler oil, or residual fuel oil, makes up 5% of refined crude oil and is used on ships, in industrial boilers and in power plants to produce electricity.
- **Asphalt and Road Oil:** Asphalt and road oil accounts for 3% of crude oil consumption.
- **Other:** Approximately 9.4% of the crude oil is refined into non-energy related feedstocks for manufacturing products such as lubricants, wax, coke for steel making, and naphthas that are used in the drycleaning process.
- **Petrochemical Feedstocks:** Petrochemical feedstocks, products of the refining process, make up the remaining 2.6% of all refined crude oil. Half of this is used to make plastics (approximately 1.3% of the total) for thousands of items such as tableware, furniture, aircraft and automobile parts, luggage, surfboards, helmets, medical supplies and packaging. The remaining 1.3% is used to make products such as solvents, synthetic fibers for wearing apparel, synthetic rubber, paints and coatings.

From a scientific and chemical perspective these refined crude oil products can be described as follows:

- **Petroleum gas** - used for heating, cooking, making plastics small alkanes (1 to 4 carbon atoms) commonly known by the names methane, ethane, propane, and butane, which is often liquified under pressure to create LPG (liquified petroleum gas).

<sup>4</sup> It should be noted that this crude oil fractionation recipe does vary by country, where differing economies require different input streams depending on the structure of their economies.

- **Naphtha or Ligroin** - intermediate that will be further processed to make gasoline mix of 5 to 9 carbon atom alkanes, and a motor fuel liquid mix of alkanes and cycloalkanes (5 to 12 carbon atoms).
- **Kerosene** - fuel for jet engines and tractors; starting material for making other products as a liquid mix of alkanes (10 to 18 carbons) and aromatics.
- **Gas oil or Diesel distillate** - used for diesel fuel and heating oil; starting material for making other products liquid alkanes containing 12 or more carbon atoms.
- **Lubricating oil** - used for motor oil, grease, other lubricants; consists of liquid long chain (20 to 50 carbon atoms) alkanes, cycloalkanes, and aromatics.
- **Heavy gas or Fuel oil** - used for industrial fuel; starting material for making other products liquid long chain (20 to 70 carbon atoms) alkanes, cycloalkanes, and aromatics.
- **Residuals** - coke, asphalt, tar, waxes; starting material for making other products solid multiple-ringed compounds with 70 or more carbon atoms.

Consistent with the nomenclature or breakdown of how a barrel of oil is used in the U.S. as previously discussed, the DOE's, Energy Information Agency (EIA) estimated the volume of oil consumption per respective product category in 2007, as shown in Table 5. The average daily oil consumption for all refined oil products in the U.S. was approximately 20.5 million barrels in 2007. Annually, total oil consumption in the U.S. is a staggering 7.5 billion barrels of oil. Keep in mind that volumetrically a barrel of oil is approximately 42 gallons. Finished motor gasoline consumption was approximately 3.4 billion barrels in 2007; multiplying a barrel of oil times 42 gallons makes the volume of finished motor gasoline consumed in the U.S. even more imposing at an estimated level of 143 billion gallons. Even with this comprehensive list of petroleum products, a barrel of crude oil can be reduced into more specialized products; that is why the term feedstock is used to explain the potential to further add value to the crude stream.

**Table 5: Volume of U.S. Petroleum Products Consumed in 2007**

	<b>Annual (Thousand Barrels Per Day)</b>	<b>Annual (Thousand Barrels Total)</b>
Finished Motor Gasoline	9,286	3,389,390
Distillate Fuel Oil	4,196	1,531,540
Liquefied Refinery/Petroleum Gases	2,085	761,025
Kero-Type Jet Fuel	1,622	592,030
Petroleum Coke	490	178,850
Still Gas	697	254,405
Residual Fuel Oil	723	263,895
Asphalt and Road Oil	494	180,310
Other Oils for Feedstocks	350	127,750
Naptha for Feedstocks	294	107,310
Lubricants	142	51,830
Miscellaneous Products	63	22,995
Kerosene	32	11,680
Special Napthas	41	14,965
Finished Aviation Gasoline	17	6,205
Waxes	11	4,015
Total	20,543	7,498,195

Source: U.S. Department of Energy, Energy Information Administration.

The final markets for value-added refined crude oil product streams are extremely large and diverse in the U.S. Table 6 highlights the estimated value of the major markets that use both petroleum and biobased feedstocks (i.e., corn and soybeans). The markets range in value from the largest market; that is gasoline at \$298 billion in 2006, down to the high emerging growth market for wood substitutes at \$3.4 billion. All of these markets use hydrocarbon based petroleum feedstocks as an input to their manufacturing activities. The petroleum content level varies significantly across markets. Gasoline and diesel are exclusively petroleum based; however, the petroleum input stream is much smaller as a percent share of the total product volume for cosmetics and personal care products.

Biobased feedstocks continue to make inroads into these different markets at a significant rate. Many companies are espousing the virtues of being green and not using petroleum based feedstock; rather, they are focused on increasing their use of renewable sources of inputs. It is unclear just how far renewable feedstocks from corn and soybeans have penetrated these markets. The easiest markets to estimate are the gasoline and diesel markets where ethanol and biodiesel production volumes are closely tracked by the industries. Less clear is an adequate understanding, for example, of the actual percent share of the sanitary cleaning products market that is biobased. Many market estimates are bantered about with little clear empirical supporting evidence, compared to such reliable surveys as the U.S. Census of Manufacturing.

**Table 6: Major U.S. Markets for Petroleum and Biobased Feedstocks, 2006**

<b>Sector</b>	<b>Value of Shipments/Markets (\$1,000)</b>
Gasoline	298,589,184
Diesel (on highway)	87,703,231
Pharmaceuticals	163,005,621
Textiles (clothing, carpets, bedding linens, auto)	38,028,266
Lubricants (motor oil, transformer fluid, hydraulic fluids, etc.)	11,308,102
Solvents	5,500,000
Sanitary Cleaning Products (hand cleaners, janitorial cleaners, household, food service, laundry)	34,267,288
Cosmetics and Personal Care Products	5,900,000
Adhesives/binders	9,230,331
Paints and Coatings (inks, paints, etc.)	22,558,703
Plastics (films, containers, polymers, insulations, foams)	203,496,075
Resins and Synthetic Rubber Manufacturing	93,499,662
Fertilizers	12,652,957
Sorbents	3,280,000
Wood Substitutes Composite Panels	3,380,000

Source: U.S. Department of Commerce: 2006 Census of Manufacturing, Freedonia Group, DOE: EIA, Informa Economics.

## 1. Conclusion

The biobased corn and soybean products and technologies will ultimately be challenged by two basic obstacles relative to petroleum; the first is economic and second is performance (attributes). The first challenge relates to the simple question: is the biobased product or technology cost competitive with traditional petro based feedstocks or related technological processes? In general, as petroleum prices rise, the easier it is to justify substituting a crude oil feedstock with a biobased corn or soybean feedstock. As petroleum prices fall the inverse is true; biobased feedstocks face inflection points in pricing where they become more costly relative to petroleum. The record high prices of crude above \$100/barrel in 2008 provided significant opportunities for biobased products to gain interest from those manufactures that were looking to replace their high cost oil feedstocks.

The second question relates to how well the respective biobased product or technology performs relative to traditional petroleum manufacturing platforms. For example, in the world of lubricants, specifically motor oil, a significant amount of

research has been conducted regarding the use of soybean oil as a potential replacement for motor oil. The challenge for soybean researchers has been to try and replicate the same qualities and characteristics of petroleum based motor oil regarding its ability to withstand high temperatures without experiencing any loss in lubricity. It is within this context that the Informa research team “set out” to indentify those corn and soybean based products and technologies that could successfully compete in terms of their relative economics and attributes compared to traditional hydrocarbon based petroleum products and technologies. It should be noted that petroleum markets have certainly played a major role in the recent interest and developments in biobased products and technologies; the growth however, has not been confined to only the large fuel markets. Significant advancements have occurred in numerous other markets because of the desirable environmental properties of renewability and biodegradability. These attractive properties are creating new and exciting opportunities for feedstocks that are based on corn or soybeans. Beyond biobased products/technologies, significant advances are also emerging in other fields like health with soy isoflavones or in more traditional ones like animal feed. Results and recommendations of this endeavor can be found in the individual commodity reports (i.e., for corn and soybeans).

### III. Overview of Top 20 Corn Products and Technologies

After assessing the products/technologies listed in Appendix A: Phase I – Corn Products/Technologies based on the criteria previously discussed (i.e., demand/market potential, economic feasibility, development stage and strength of institutional support), the top 20 products/technologies were identified. These products/technologies are briefly reviewed within this section and are listed in Table 7. Upon further analysis and interviews, this list was then further refined down to the top 8, which are each presented in more detail within the next section (IV. Top 8 Corn Products/Technologies).

**Table 7: Top 20 Corn Products and Technologies**

Product/Technology Name	Product/Technology Timeframe
<b><u>Ethanol Process Improvements and Co-Product Utilization</u></b>	
Anaerobic Digestion	Medium
Back-End Corn Oil Extraction	Short
CO <sub>2</sub> in Algae Production	Long
Ethanol Distillation	Medium
Front-End Fractionation	Short
Microwave Drying of Distillers Grains	Short
Reactive Distillation	Short
Supercritical Carbon Dioxide Corn Oil Extraction	Medium
Zein Extraction	Medium
<b><u>Second Generation Biofuels</u></b>	
Butanol	Medium
Cellulosic Ethanol - Biochemical Platform	Medium-Long
Cellulosic Ethanol - Thermochemical Platform	Medium-Long
<b><u>Value Added Chemicals</u></b>	
3-Hydroxypropionic Acid	Long
Itaconic Acid	Long
Levulinic Acid	Long
Lignin - Aromatics	Long
Polylactic Acid	Short
1,3-Propanediol	Short
Sorbitol/Isosorbide	Short-Long*
Succinic Acid	Medium

\*The commercial production of sorbitol is well established . However, technology developments to improve the sorbitol production process and to produce derivative chemicals such as isosorbide are under development.

Short term: 0-3 years

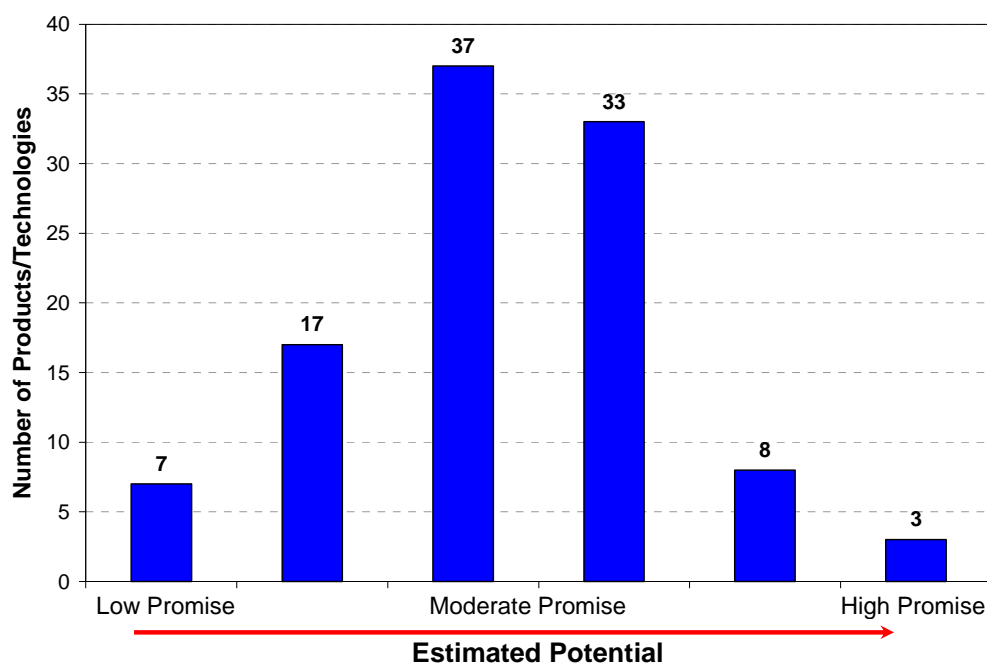
Medium term: 3-5 years

Long term: > 5 years

It is important to keep in mind that this list is ever changing, as new developments are brought forth and as new information about these technologies is realized. These products and technologies have the potential to move in either direction, up or down the list of top prospects.

Each of the 100+ products and technologies were assessed based on their demand/market potential, their economic feasibility, their stage of development, and their strength of institutional support. The distribution of the assessed potential for the reviewed products and technologies is presented within Figure 17. As illustrated, 11 of the top 20 were assessed as having a high degree of promise; however, the decision regarding which of the other 9 to include in the top 20 was more subjective. This is where the value in the interviews with generalists in the field of biobased products and technologies was truly realized. These interviews helped to provide confirmation and insight into the finalization of the top 20 list.

**Figure 17: Distribution of Corn Products/Technologies Based on their Estimated Potential**



While the process utilized to reach the top 20 was designed to identify those products and/or technologies which are considered to have the greatest potential to add significant value to Minnesota's corn commodity production, the value in many of the remaining products and technologies (listed in that Appendix A: Phase I – Corn Products/Technologies) should not be entirely overlooked. For instance, there is often a trade-off between “big bang” technologies – those with potentially large demand effects - and those products and technologies that may not have the “big bang” effect but are less capital intensive. Based on the review process and the scoring weights that were placed on products and technologies considered to have

potentially large demand effects, many of the products and technologies deemed to have a smaller demand impacts did not make the top 20 list. Yet, many of these smaller demand impact products and technologies are less capital intensive and they may be more obtainable/suitable for certain companies or institutions, particularly in the short-term.

Many of the identified top 20 products and technologies are energy related products/technologies. These could constitute either technologies that improve upon the economics of existing corn-to-ethanol production processes (these are presented in Appendix B: Traditional Corn-to-Ethanol Production Processes) or “new” energy products such as butanol and cellulosic ethanol. Energy markets are large and energy prices have been high. These high prices, along with environmental concerns have driven governments around the world, and the U.S. in particular, to push for the development of renewable fuels. This push has come in the form of mandates as well as increased funding for research and development.

One additional thing to keep in mind when reviewing the products and technologies identified throughout all phases of this report is that many are centered around the utilization of the sugar components within corn. Depending on the individual technology, this sugar can be from the 6-carbon sugar glucose that is produced from starch found within the corn kernel; the glucose and 5-carbon sugars, such as xylose, that are found in the lignocellulosic biomass of corn (e.g., corn fiber, corn stover and corn cobs); or from other sugars such as sucrose or fructose. The caveat that should be kept in mind throughout all of this is that corn is not the only source of sugar, and many of the reviewed technologies can also utilize sugar from other feedstocks. Which feedstock is utilized by the given technology will come down to regional economics - which is the cheapest sugar source within a given area.

## **A. Ethanol Process Improvements and Co-Product Utilization**

Given the large and growing ethanol market and its impact on corn demand, as well as the existing infrastructure already established within the state of Minnesota, products/technologies designed to improve the production economics of traditional corn-to-ethanol processes were generally weighted favorably throughout the review of emerging products and technologies in phase I. Throughout the remainder of this report, when discussing the benefits of these new technologies, references are often made in relation to how said technology differs or improves upon the traditional corn-to-ethanol production process. This being the case, Appendix B: Traditional Corn-to-Ethanol Production Processes provides an overview of current ethanol production processes.



## 1. Anaerobic Digestion

Anaerobic digestion uses bacteria to convert the thin<sup>5</sup> or whole stillage by-product of ethanol production into biogas – a mixture of methane (50-80%), CO<sub>2</sub> (20-50%), and trace amounts of H<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>S, which can be burned for energy as a substitute for natural gas. This process reduces energy costs and greenhouse gas emissions and helps to conserve water relative to traditional corn-to-ethanol production. Furthermore, if collected, the struvite, a sludge that builds up in the digester, could be sold as a valuable fertilizer or a livestock feed additive, as it is composed of magnesium, phosphate, and ammonia. Additionally, if the final rulemaking for the Renewable Fuel Standard established under the Energy Independence and Security Act of 2007 (only the proposed rulemaking has been issued as of the writing of this report), anaerobic digestion will provide a mechanism for an ethanol facility to reduce the greenhouse gas “score” associated with its ethanol output. However, these benefits should be weighed against a possible reduction in revenues from the co-product sales of distillers grains, depending on whether whole or thin stillage is utilized.

It is estimated that anaerobic digestion using thin stillage can reduce the energy needs of an ethanol facility by 43-66%, and if using whole stillage, energy needs could be entirely met by the biogas.

According to an August, 2008 article in *Technology Review*, University of Minnesota research fellow Douglas Tiffany says that the challenge with anaerobic digesters is the expertise required to maintain a stable bacterial community at high temperatures and avoid system crashes. Additionally, according to Otter Tail Ag Enterprises' CEO Kelly Longin, the up-front costs of the technology would be at least \$20 million for their 55 mmgy dry-mill ethanol facility (2008). Yet, despite its drawbacks, its potential has spurred the interest of several large companies and research universities, and research and development efforts to improve the anaerobic digestion process of corn ethanol thin and whole stillage are ongoing.

POET recently began using an anaerobic digester at its cellulosic ethanol pilot plant in Scotland, SD, which uses corn cobs as its primary feedstock. The anaerobic digester is being used to power the cellulosic plant and offset natural gas usage at its attached grain ethanol plant. Another cellulosic ethanol company looking to incorporate an anaerobic digester is BioGasol; Canadian ethanol producer Kwartha Ethanol is doing so as well.

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<sup>5</sup> Thin stillage is the solubles portion of whole stillage (the liquid fraction that remains after the ethanol has been removed), which is generally evaporated to produce condensed distillers solubles and is often added back to the distillers grains to become distillers grains with solubles.

## 2. Back-End Corn Oil Extraction

The basic corn oil extraction technology involves a centrifuge process to separate the oils from the corn stillage. By removing the oil from the distillers grains, the ethanol facility not only captures an additional revenue stream from the extracted corn oil, but also reduces their distillers grains drying costs and associated greenhouse gas emissions, while still producing a marketable co-product in the form of low fat distillers grains<sup>6</sup>. However, in comparison to front-end oil extraction processes (see Section III.A.5 “Front-End Fractionation”), the oil extracted from the back-end is a lower-value product, as it cannot be used in food applications. The trade-off is that the technology is ready now and is already being used in several commercial ethanol facilities and the capital cost requirements are much lower.

GreenShift and Primafuel are two companies currently offering back-end corn oil extraction technologies to ethanol facilities. Both companies are offering packages where they supply the capital for building the process in return for an oil buy back agreement. Greenshift prices the oil off of an index which is based on the price of diesel fuel. They then use the oil they purchase to supply their biodiesel refinery in Adrian, Michigan.

A recent analysis conducted by the U.S. Environmental Protection Agency showed that the process increased the yields of biofuel from corn by 7% (e.g., when oil is used for biodiesel production) and reduces the amount of fossil fuel used in the ethanol production process by 10%. Based on USDA economic analysis, the capital cost to install the GreenShift corn oil extraction system in a 50 mmgy facility would be \$6 million.

While this technology is already commercialized, process developments are ongoing. For example, Iowa State University is researching ways to increase the quantity of oil removed via centrifugation, and Primafuel Solutions announced in an August 2008 *Ethanol Producer* article that they were planning on introducing additional bio-separation innovations in 2009.

## 3. CO<sub>2</sub> in Algae Production

CO<sub>2</sub> is a current by-product of ethanol production that only a limited number of ethanol facilities are able to sell it due to the geographic concentration and size of the ethanol industry relative to the gas industry's needs. In some cases, it is used by the soft drink industry as a source of carbonation, or by other food processors (e.g., quick freeze applications), but in many cases ethanol facilities simply release it into the atmosphere. Any further value that could be received from this product stream would improve the economics of ethanol production, if the value were to justify the costs associated with its capture. Additionally, with legislation under

<sup>6</sup> Yet, while low fat, high protein distillers grains may be desirable for some markets, it is not desirable for all (e.g., it is more beneficial for beef, dairy and possibly swine than for poultry).

consideration for cap-and-trade implementation, there may be even greater economic incentive in the future for ethanol producers to reduce the amount of CO<sub>2</sub> that is released into the atmosphere.

One potential use of CO<sub>2</sub> is in the production of algae. The CO<sub>2</sub> emitted from the ethanol production process can be captured and used as a key input (via photosynthesis) in the production of algae, which is in turn used to produce oil. , Many algae technology developers are targeting the production of “biocrude”, which is essentially algae oil that can be cracked or refined just like crude oil into traditional petroleum products such as gasoline, diesel, jet fuel, heating oil, or other chemicals.

Today, there are many companies/institutions developing algae production systems and there is strong financial backing from both the public and private sectors. There is also a wide array of distinct process technologies being developed. Furthermore, according to the National Renewable Energy Laboratory (NREL) representatives, off-take of CO<sub>2</sub> from an ethanol facility would be of a quantity complimentary to the needs of a commercial scale algae operation. However, algae production is not yet commercially viable, and is not likely to be commercialized within the next 5 years.

#### **4. Ethanol Distillation**

Energy costs currently account for about 12% of overall operating costs of traditional corn-to-ethanol production, the second largest operating cost next to feedstock costs. Of the overall energy consumption, distillation and dehydration consume about 50% (McAloon et al., 2004; Kim and Dale, 2005 – cited by Vaperma). It is also one of the key cost components in the biochemical cellulosic ethanol platform. However, several alternative ethanol distillation technology developers claim to achieve a 40% reduction in energy costs over traditional distillation methods, this would equate to an approximate 6¢ per gallon cost savings or \$3 million per year for a 50 mmgy ethanol facility (using current natural gas prices). Additionally, according to one technology developer, Vaperma, if using their process, overall fuel production could also be increased by 20% through reductions in process bottlenecks that increase plant throughput/capacity.

Traditionally, the separation of ethanol and water is performed through a combination of steam distillation and a molecular sieve. However, there are various processes being developed whereby ethanol is removed during fermentation, reducing product inhibition and energy costs, and thereby also reducing greenhouse gas emissions. Alternative ethanol distillation technologies currently being developed include: vacuum stripping, gas stripping, membrane separation, solvent (liquid) extraction, and supercritical CO<sub>2</sub>.

While each of these methods has its own pros and cons, the leading technology at this time appears to be membrane separation, currently being pursued by Vaperma (Siftek) and Whitefox Technologies. This technology uses membranes, which are

vapor phase separation units, to allow the preferred permeation of water over other vapor components in a gas mixture. The removed ethanol is then distilled and the remaining fermentation broth is recycled.

Another ethanol dewatering technology is MOR Supercritical's supercritical CO<sub>2</sub> process, which has the added benefit of CO<sub>2</sub> utilization. The company claims that their process is economically competitive with proposed membrane technologies.

These technologies are largely in the late development/early commercialization stage, and are expected to reach commercial status within 3-5 years, if not sooner.

## **5. Front-End Fractionation**

There are several front-end fractionation processes that separate the corn entering into the dry-mill ethanol facility into three fractions: pericarp (bran/fiber), germ (the oil-bearing portion of the kernel) and endosperm. Revenue streams generated from this process include corn oil; high protein, low fat and fiber distillers grains; bran/fiber and ethanol. Additionally, according to some technology developer claims, front-end fractionation can reduce energy consumption and lower volatile organic compound emissions. And while there are also back-end fiber and oil extraction technologies that are either currently available or being developed that are less expensive, these processes do not produce the high value co-products that are generated from front-end fractionation. Additionally, there are ethanol production efficiencies that are gained when the starch fraction is separated out at the beginning of the process.

Front-end fractionation technologies can generally be classified as either wet fractionation processes (e.g., Quick Germ Quick Fiber, Enzymatic Milling, CVP's HydroMill) or dry fractionation processes (Cereal Process Technologies, Delta-T/Ocrim Milling, Crown Fractionation System, Renessen-Extrax Processing System, POET's BFRAC system). While there are numerous companies, each with slightly different technologies, there are a few basic pros and cons that can be identified between the wet and dry fractionation technologies for modified dry-mill ethanol plants. In general, wet fractionation technologies tend to be more costly. However, they also produce higher-valued co-products and have less starch loss than dry fractionation technologies. The germ extracted by wet fractionation technologies has an oil content of approximately 40+% compared to 20-25% from typical dry fractionation technologies. This low oil germ produced by dry fractionation is sometimes referred to as "dirty germ," and often oilseed processing facilities or wet mills are not geared to take germ with this low of an oil content. Yet, because corn oil extraction equipment is currently considered cost prohibitive and many companies do not want to handle hexane, ethanol producers typically do not want to extract the oil themselves. Additionally, the higher starch loss associated with the dry fractionation technologies is a revenue factor for the ethanol producer, as ethanol yields are compromised. Nonetheless, dry fractionation technologies are more prevalent in current plant installations, primarily due to cost differences.

The company MOR Technology claims to have developed a unique fractionation process known as MOR FRAC+, with costs similar to those generally associated with dry fractionation technologies, but with the higher valued co-products and the lower starch loss generally associated with wet fractionation technologies. MOR is currently working with a number of customers, design-build firms and financing institutions to install the technology in corn-based ethanol plants. While unproven at a commercial scale, this process appears to have promise.

## **6. Microwave Drying of Distillers Grains**

Microwave drying technology is an alternative to conventional rotary drum gas dryers used to dry the ethanol by-product, distillers grains. There are several companies currently pursuing the development and commercialization of this technology. The most commonly reported company supplying this microwave drying technology is Cellencor. Yet, based on an interview with John Caupert, director of the National Corn-to-Ethanol Research Center (NCERC), there have been multiple other companies interested in pursuing the development of this technology. However, the names of these companies were withheld due to non-disclosure agreements with NCERC.

Microwave drying technology works by vibrating the water molecules within the distillers grains, creating friction which converts radio energy to heat energy and vaporizing the water molecules; because the protein and fiber in distillers grains do not readily absorb microwave energy, they do not heat up as much and the product is kept cooler. Additionally, according to technology developer Cellencor, microwave dryers typically have a 90% energy efficiency compared to about 50% for gas rotary dryers.

Cellencor claims that their microwave drying system significantly reduces process energy consumption, enhances the value of animal feed co-products, reduces air emissions, potentially reduces water usage, and is safer and more reliable than current drying systems. Animal feed co-product value is enhanced as microwave drying systems avoid the protein and amino acid damage that results from the high temperatures of conventional gas dryers. The company also has a patented enzyme enhancement process whereby the activity of enzyme additives is enhanced when the structure of the cellular walls is broken down by the microwave energy, resulting in an animal feed with higher available energy. Additionally, the system is electrically powered and uses one-half to one-third of the BTUs per pound of water removed than conventional gas dryers. An added benefit of electric powered drying systems is that they avoid the price volatility of natural gas. The company claims that the system could save ethanol producers 20% or more in operating costs and that the payback period for installation would be 2-5 years.



The Cellencor system has been field tested in both wet and dry mill ethanol facilities, including at Corn Plus in Minnesota in the spring of 2008. Additionally, according to a May, 2009 article in "Biofuels Canada", Kawartha Ethanol, Inc, plans to use a microwave drying process in their 80 mmgy plant in Havelock, Ontario.

## **7. Reactive Distillation**

While inorganic catalysts have long been known as a method to produce valuable chemicals in the petroleum industry, their application on corn-based feed streams has up until now been cost prohibitive due to challenges associated with separating the mixture of chemicals that are derived from such a feed stream with multiple compounds. However, the reactive distillation process can successfully separate a mixed stream of different chemicals by treating that stream with a reactive chemical in the presence of a catalyst, resulting in a mixture of chemicals that can be easily separated.

One of the challenges facing both corn starch-based ethanol and cellulosic ethanol producers is that while the fermenting agent is producing ethanol, other unwanted acid by-products are also being produced. These by-products are often difficult to separate out of the mixture. And while many current research efforts are focused on minimizing the production of these acids, this technology is designed to separate out these acids from the ethanol in such a way that would allow an ethanol or cellulosic ethanol facility to produce a valuable co-product. For example, Michigan State University (MSU) researchers are currently focusing on the production of ethyl lactate from lactic acid and ethanol. Ethyl lactate is a general, all-purpose solvent as well as a common input in pharmaceuticals, food additives, and fragrances. Today, ethyl lactate is not commonly used due to its high production costs. In 2007, the cost of producing ethyl lactate was \$1.30-1.60 per pound (Carl Lira, MSU). However, researchers claim that they have cut this cost in half using reactive distillation. The National Corn Growers Association is currently seeking ethanol companies interested in purchasing a license for this technology to be retrofitted into an existing dry-grind ethanol plant.

## **8. Supercritical CO<sub>2</sub> Corn Oil Extraction**

Rather than using hexane, MOR Supercritical's technology uses carbon dioxide as the only solvent in their process to extract corn oil from germ and vegetable oil from oilseeds. As opposed to conventional supercritical processes, MOR Supercritical claims that their technology greatly reduces operating costs which have prevented other supercritical systems from replacing petrochemical extraction using hexane. MOR Supercritical claims that their technology is energy efficient; automated, modular and scalable; has a small environmental footprint (1/6 of a typical solvent extraction plant); produces safe, solvent-free, non-degraded, high-quality products

including undegraded meal with high protein digestibility; and can be paired with an accompanying refining technology to extract and refine the oil in one step.

This system can be coupled with MOR Technology's fractionation system (MOR-FRAC Plus+) to provide added value for ethanol facilities or installed as a stand alone facility to produce high quality specialty oils, bioactive ingredients, or nutraceuticals. It can also be used to extract oil from algae. Additionally, the technology can be applied to ethanol dehydration. While the success of separating alcohol and water via supercritical fluids has been demonstrated for many years, these previous demonstrations have not been able to compete with the economics of traditional steam distillation methods or other methods such as membrane separation. However, MOR Supercritical claims their process is scalable and cost-efficient relative to other proposed dehydration technologies.

MOR Supercritical is currently building a 15 ton/day oil extraction plant in Pennsylvania that is expected to be completed by the 3rd quarter of 2009. Afterward, they plan to offer their technology to commercial plants at initial volumes of up to 300 tons/day. Meanwhile, MOR is also working with a number of customers, design-build firms and financing institutions to install their fractionation technology (which can be coupled with the CO<sub>2</sub> oil extraction technology) in corn-based ethanol plants around the country.

## 9. Zein Extraction

Various processes have been developed to extract zein protein from corn and corn by-products (e.g., DDGS). Zein is a high-value protein which can be used in a wide range of applications. Zein is not used extensively in human food products, despite being edible, due to its negative nitrogen balance and poor water solubility. However, this insolubility is what makes zein and its resins form tough, glossy, hydrophobic grease proof coatings that are resistant to microorganisms, heat and humidity. Zein applications include: specialty coatings for pharmaceutical tablets, candies, nuts, and paper products; chewing gum; adhesives and binders; inks; cosmetics; fibers and textiles; resins and biodegradable plastics and high-value biomedical applications.

Currently, zein can be extracted from corn gluten meal, a by-product of the wet milling process. However, current extraction and purification technologies are such that the price of zein limits current market applications. Zein is currently a high value product. According to various sources, purified zein prices range from \$4.54-\$32 per lb, depending on the level of purification and quality. With a cited yield of 0.8 lbs of zein per bushel of corn, zein revenues could potentially exceed that of ethanol if implemented into a corn-to-ethanol facility. However, the big question is cost. While a December 2008 article in *Ethanol Producer Magazine* stated that there is currently no cost-effective way to recover and purify zein protein, there are several companies and research institutions currently working to develop technologies to bring these



extraction and purification costs down, including the University of Nebraska, Lincoln; Purdue University; University of Illinois; Iowa State University; Prairie Gold; USDA, Agricultural Research Service (ARS); Global Protein Products, Zea Fuels and Bio Process Innovations.

## **B. Second Generation Biofuels**

The demand for cellulosic ethanol is in part supported by the Renewable Fuel Standard established by the Energy Independence and Security Act of 2007, which contained a 21 billion gallon mandate for advanced biofuels by 2022, including 16 billion gallons of cellulosic biofuel. Some cellulosic biofuel companies are focused on feedstocks other than corn which offer greater environmental benefits and less impact on prices of major agricultural commodities; yet, corn biomass (e.g., corn stover, corn cobs, and corn fiber) will likely have a place in the mix of future feedstocks. Given the volume of ethanol that can be produced from corn starch and the interest in corn biomass as a cellulosic feedstock, this emerging technology has the potential to have a large demand impact on the corn industry.

Butanol is another second generation biofuel that is currently being developed which could potentially be used as an ethanol replacement, an ethanol substitute, or in the manufacture of traditional petrochemically based fuels, such as gasoline, diesel, and jet fuel.

### **1. Butanol**

Butanol is a 4 carbon alcohol currently produced via petrochemical feedstocks and used primarily as an industrial solvent. In 2007, the worldwide butanol market was estimated at about 350 mmgy, with the U.S. accounting for 220 mmgy (*Ethanol Today*, March 2007). Yet, if cost competitive, butanol could also be produced via fermentation of sugars (including sugars derived from corn starch) and could function as an alternative renewable fuel, expanding the market to several billion gallons. Butanol has several key advantages over ethanol, including its higher energy content, its ability to be transported via pipeline, its lower Reid vapor pressure which makes it safer to use and means that it generates fewer volatile organic compound emissions, and higher allowable blend levels with gasoline.

While there are several different butanol production processes being developed, essentially the process is very similar to the ethanol production process, as any ethanol facility can be retrofitted to produce biobutanol, and cellulosic ethanol technology developments currently underway can also be applied to butanol production. Rather than using the ethanol producing yeast, a butanol producing microorganism is used to ferment the sugars from corn (or any sugar feed source, including cellulosic biomass) to produce butanol. However, more recent challenges facing developers have been largely in the area of reducing distillation costs and

there will likely have to be alterations made to an ethanol facility's distillation process in order to produce butanol. There have been many advancements made to the biobutanol production process over the last several decades and many of the challenges previously preventing biobutanol production from being economically viable have largely been resolved. The technology appears to be currently cost competitive with petrochemical based butanol (said to be economical at \$60/bbl crude oil) and also competitive or nearly competitive with ethanol.

There are many companies and research institutions working on the development of commercial biobutanol production, including BP and DuPont. Of those companies currently pursuing its development, the earliest stated year for expected commercial biobutanol production is 2010, but many do not expect to see commercial scale production until 2011/2012.

## **2. Cellulosic Ethanol – Biochemical Platform (Pretreatment, Hydrolysis, and Fermentation)**

There are two main technology pathways currently being developed for the production of cellulosic ethanol from lignocellulosic feedstocks: biochemical and thermochemical. There have been significant investments made in the development of both of these production routes, and commercial scale facilities have been proposed and are beginning to be built

Over the past few years, there has been significant research and development efforts given toward improving the high production cost areas of biochemical cellulosic ethanol production: pretreatment<sup>7</sup>, hydrolysis, and fermentation<sup>8</sup>. There are essentially three key challenges involved in these processing steps. The first is the development of cost efficient pretreatments, which are necessary in order to open up the structure of the biomass sufficiently to allow for effective hydrolysis. Once the sugars are hydrolyzed, broken down into 5-carbon and 6-carbon sugars, they can then be fermented using biological agents (e.g., microorganisms, yeast) to produce ethanol. However, it is far more difficult, and thus more costly, to hydrolyze cellulosic biomass than it is to hydrolyze the starch from the traditional corn-to-ethanol process, and that while hemicellulose is relatively easy to hydrolyze compared to cellulose (fractions of the lignocellulosic biomass<sup>9</sup>), it is more difficult to ferment. Therein lies challenges two and three: hydrolyzing the cellulose and fermenting the xylose sugars released from the hemicellulose.

<sup>7</sup> The pretreatment of biomass is currently one of the single largest cost components in the overall cellulosic ethanol production process via the biochemical platform, accounting for 19% of the overall cost, second only to raw material costs (NREL, May 2007 presentation).

<sup>8</sup> Distillation costs are another large cost component to the overall process, and distillation and dehydration technology developments being made for the traditional corn-to-ethanol process will also apply to cellulosic ethanol processes. See section III.A.4 "Ethanol Distillation" for more details.

<sup>9</sup> Corn stover is composed of approximately 36.0% cellulose, 23.4% hemicellulose, and 18.6% lignin (Dien et al., 2006).

There are numerous companies and research institutions developing their own approaches and unique technologies to improve upon current pretreatment, hydrolysis and fermentation processes. However, the bottom line is that a cost efficient process has yet to be commercialized. There are several companies that are expecting to reach commercialization by 2011/2012. Yet, the tight capital market is inhibiting many from obtaining the capital needed to go forth with their commercialization efforts.

### **3. Cellulosic Ethanol – Thermochemical Platform**

Pyrolysis/gasification technologies are used to produce pyrolysis oil/syngas, from which a wide range of long carbon chain biofuels and chemicals can be reformed. In contrast to the biochemical platform, the thermochemical platform is largely based on existing technologies used within the petroleum industry and there appears to be fewer technical hurdles. Although, being a more mature technology, there may also be fewer opportunities for cost reductions.

Gasification is the process of heating biomass by partial oxidation or in the presence of steam to produce a mixture of carbon monoxide and hydrogen called synthesis gas or syngas. The syngas is then cleaned before being passed through the Fischer-Tropsch process to create fuels or chemicals. Research and development efforts are focusing on perfecting the gasification of biomass so that it is more reliable and cost efficient. One of the major technical challenges is that much of the syngas produced from biomass tends to be more heterogeneous than petroleum-based syngas, leading to variations in product quality. Also, the number of inhibitory substances vary by biomass feedstock and gasifier design. This variation in syngas composition creates problems for the Fischer-Tropsch process, including low product selectivity and unavoidable co-products, as well as contaminants which can inhibit the catalytic reaction. Additionally, the large quantity of biomass required to reach a scale where the process is economical remains a concern. Larger scale requires feedstocks to be brought in from greater distances, which erodes economic competitiveness.

Pyrolysis is the process of heating biomass in the absence of added oxygen to decompose the biomass and produce a liquid called pyrolysis oil. This oil is generally quite unstable to viscosity changes and oxidation, which makes its use as a chemical or a fuel problematic. Therefore, it must first be pre-treated and stabilized prior to its incorporation into petroleum refinery processes. Research efforts focus on preconditioning the oil before stabilization, catalyst and process developments to stabilize the pyrolysis oil, and validation of the compatibility of the stabilized oil with current petroleum conversion catalysts and processes.

Both gasification and pyrolysis could be incorporated into a thermochemical biorefinery or a biochemical biorefinery. There are several companies currently

pursuing the commercial development of cellulosic ethanol via the thermochemical platform; however, commercial viability is yet to be proven.

## **C. Value-Added Chemicals**

There are many chemicals that can be produced from corn and other sugar sources. These chemicals can then be used in the production of a wide array of biobased products. In general, the biobased product industry is growing as more and more consumers are showing preference for non-petroleum based products and as the general product markets grow, driven by the steadily increasing world population and rising income levels. Additionally, programs such as LEED<sup>10</sup> and USDA BioPreferred<sup>11</sup> also help stimulate biobased product demand.

However, in order for a biobased chemical to gain any significant share of the petroleum based chemical market, it must also be cost competitive with similarly functioning petroleum based chemicals. There are currently significant research and development efforts underway to find biobased production routes that are economically competitive with traditional petrochemicals.

In 2004, a U.S. Department of Energy (DOE) report identified 12 of the top value added chemicals that can be produced from sugars and synthesis gas, beginning from a list of more than 300 candidates. These 12 were identified by examining the potential markets of the chemicals and their derivatives, as well as the technical complexity of their synthesis pathways. The value added chemicals presented in this top 20 list were in part identified based on further analysis of these top 12 chemicals. However, other chemicals were also included based on information gathered from desk research and interviews with industry experts, as it related to the previously established evaluation criteria.

### **1. 3-Hydroxypropionic Acid**

3-Hydroxypropionic acid (3-HPA) is a building block chemical that can be used to produce many other commodity and specialty chemicals used in a wide array of product applications, including solvents, plastics and moldings, fibers and resins, composites, adhesives, coatings, aliphatic polyesters and copolyesters, and disinfectants. One of the most promising aspects of this building block chemical is not only the current petrochemical products which it could potentially replace, but also the new and unique chemical properties it would bring to the market. Given its

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<sup>10</sup> LEED (Leadership in Energy and Environmental Design) is third-party certification program for the design, construction and operation of high performance green buildings. Qualifying for LEED credits can qualify a company for tax rebates, zoning allowances and other financial incentives.

<sup>11</sup> USDA's BioPreferred program includes a preferred procurement program for Federal agencies and their contractors, and a voluntary labeling program for the broad scale consumer marketing of biobased products.

potential, it was identified by the U.S. DOE in 2004 as one of the top 12 chemicals from biomass sugars and syngas.

There is currently no commercially viable production route for 3-HPA using petrochemical feedstocks. However, many of the derivative chemicals that can be produced from 3-HPA are commercially produced from fossil fuel feedstocks. Cargill, along with Codexis and the Pacific Northwest National Laboratory (PNNL), have already developed a bioprocess to produce 3-HPA which converts glucose or other carbohydrate sources into 3-HPA using a multi-step enzymatic reaction within the cells of a microorganism. 3-HPA can then be converted into a variety of high-value chemicals, including acrylic acid, 1,3-propanediol, malonic acid, and acrylamide. In early 2008, Cargill announced a joint agreement with Novozymes to develop technology enabling the production of acrylic acid via 3-HPA, supported by a \$1.5 million matching cooperative agreement from the DOE. At the time of the announcement, the companies said that they expected their technology to produce 3-HPA and its derivatives, such as acrylic acid, to be ready in 5 years. According to a 2005 DOE presentation, acrylic acid production via this biochemical route could result in an advantage of more than 5 ¢/lb over propylene oxidation for a Midwest plant (West Texas Intermediate crude oil 2005 average = \$56.5/bbl).

However, through personal communication, Cargill has revealed that they no longer plan to pursue the development of 3-HPA, as they do not feel that they have the expertise required to “bring profitability in a reasonable time.” This would indicate that this product/technology is more likely a long-term prospect.

## 2. Itaconic Acid

Itaconic acid is a building block chemical that can be produced by sugar fermentation and used to derive many other high-value chemicals. Itaconic acid derivatives include 3- & 4-Methyl- $\gamma$ -Butyrolactone, 3-Methyl Tetrahydrofuran, and 2-Methyl-1,4-Butanediol, among others. These derivatives yield new properties for the butanediol (BDO),  $\gamma$ -butyrolactone (GBL), and tetrahydrofuran (THF) family of polymers. Applications of itaconic acid include paper coatings, carpet backings, medicines, cosmetics, lubricants, herbicides, solvents, acrylic fibers and rubbers, reinforced glass fiber, artificial diamonds and lenses, and as a potential component of P-series fuels<sup>12</sup>. Itaconic acid was also identified by the DOE in 2004 as one of the top 12 chemicals from biomass sugars and syngas.

The base technology for the fermentation of itaconic acid is commercialized, but research efforts on efficient, low cost methods for the production of itaconic acid and its derivatives are ongoing. According to a 2001 study, the itaconic acid market was 15,000 tons/year and the selling price was \$4/kg. According to a Netherlands company, TNO Quality of Life, the production potential of itaconic acid has been

<sup>12</sup> According to the DOE a “P-Series fuel is a blend of natural gas liquids (pentanes plus), ethanol, and the biomass-derived co-solvent methyltetrahydrofuran

inhibited by the fact that the genes involved in the biosynthesis of itaconic acid have not been well-known. However, the company claims to have identified three genes crucial to the microbial production of itaconic acid. Additionally, in a USDA, ARS project aimed at finding new microbial processes for using glycerol and the effect of various reaction parameters to produce new compounds, a new fungal strain was incidentally found that can use glucose or maltose sugars (but not glycerol) to produce itaconic acid. This process has since been patented.

### **3. Levulinic Acid**

Levulinic acid is another building block chemical from which many other high-value chemicals can be derived, and was also identified by the DOE in 2004 as one of the top 12 chemicals from biomass sugars and syngas. Potential applications from levulinic acid and its derivative chemicals include, but are not limited to, food/beverage acidulants, synthetic rubbers and plastics, pharmaceuticals, solvents, coatings, herbicides and pesticides. In addition to being a building block chemical for many other high-value chemicals, levulinate esters (85%) mixed with other alcohols (e.g., ethanol, methanol, butanol) produce a desirable fuel product. Levulinate esters produce a clean burning fuel (burns cleaner than pure hydrocarbon products) that can be transported via pipeline, has a low cloud point in diesel blends (lower than biodiesel), has a higher fuel efficiency than ethanol, reduces soot, and exceeds ASTM D-975 standards.

Maine BioProducts' Biofine process is a thermochemical process using acid hydrolysis to produce levulinic acid and other co-products (e.g., furfural, formic acid, and char) from cellulose. The company intends to focus on the fuel market, stating that the high value, low volume chemicals do not yield the profit needed to justify the construction of a full sized plant. For this reason, the strategy of Maine BioProducts is to co-locate their Biofine process along with existing/future bio-alcohol supplies (e.g. ethanol, cellulosic ethanol, butanol). The company claims that even with co-location, the initial investment will be in excess of \$120 million.

Processes are still being developed to produce derivatives from levulinic acid, and some of these processes are further along than others. The PNNL and NREL have developed and patented a process ready for licensing to produce methyl tetrahydrofuran (ME-THF) from levulinic acid. ME-THF is a potential component of P-series fuels<sup>12</sup> and has been demonstrated to be a useful replacement for the solvent tetrahydrofuran. They are also developing, although at a less advanced stage, a process to produce delta-amino levulinic acid, an active chemical in a new group of herbicides and pesticides.



#### 4. Lignin - Aromatics

Lignin accounts for 18.6% of corn stover biomass (Dien et al., 2006), and currently, the proposed value of lignin in a cellulosic biorefinery is largely limited to its value as a boiler fuel to supply power for the plant. However, conceptual and early stage research is exploring cost efficient methods to produce high-value chemicals from lignin, which would help increase the overall revenues of the cellulosic biorefinery. According to the PNNL, "lignin is the only renewable source of an important and high-volume class of compounds - the aromatics." U.S. demand for three of the largest aromatics; BTX (benzene, toluene, and xylene), phenol, and terephthalic acid, is approximately 27.9 million metric tons per year. This class of chemicals can be found in a wide range of consumer products, including pharmaceuticals, synthetic rubbers, upholstery, clothing, plastics, various car parts (e.g., body, bumpers, lighting, dashboard, seats, upholstery, fuel systems, under-the-bonnet components) and CDs/DVDs. Yet, despite its demand potential, this long-term technology has some significant technical barriers it must first overcome and is not likely to be commercialized within the next 5 years.

#### 5. Polylactic Acid

Polylactic Acid (PLA) is a thermoplastic derived from lactic acid, a fermentation product produced from biomass sugars. PLA is currently commercially produced from corn feedstocks at Cargill's 140,000 MT/yr facility in Blair, Nebraska. However, full market penetration has not been reached and Cargill projects a possible market of 3.6 million metric tons by 2020. Yet, they are not the only ones that are optimistic. A recent (August 2008) study by the Freedonia Group estimated that PLA demand will expand by nearly 20% between 2008-2012.

Cargill markets their PLA as Ingeo™ through the company NatureWorks. Ingeo biopolymers and biofibers have many market applications, including packaging (e.g., high-value films, rigid thermoformed food and beverage containers, and coated papers and boards), apparel, carpet, furnishings (e.g., drapery, panel and wall covering, and bedding), non-wovens (e.g., diapers, baby and facial wipes and feminine products), and industrial textiles (e.g., geotextiles, agrotexiles and specialist filtration media).

Cargill claims that their PLA production technology is cost competitive with conventional polymers, and that the PLA produced has many performance properties equal to or greater than conventional polymers such as polyethylene terephthalate (PET) and nylon. Additionally, PLA is biodegradable. Since its commercial launch in 2002, the company has made improvements to its process that have further reduced CO<sub>2</sub> emissions and reduced process energy requirements. According to the Institute for Energy and Environmental Research in Heidelberg, Germany, the new Ingeo resin emits 77 percent less CO<sub>2</sub> than PET. The company



is also looking to develop fermentation organisms to convert 5-carbon sugars as well as glucose into PLA.

## 6. 1,3-Propanediol

1,3-propanediol (PDO) is a commercially produced building block chemical commonly used in the production of polymers. DuPont Tate&Lyle BioProducts is the primary producer of this bio-chemical, producing Zemea™ propanediol and Susterra™ propanediol from corn glucose. Their Bio-PDO plant is located in Loudon, TN, and has an annual production capacity of 100 million pounds. However, the market potential for Bio-PDO is estimated to be quite a bit higher. Currently, PDO is primarily produced from chemical feedstocks (e.g., ethylene oxide or propylene) and is a chemical precursor to polytrimethylene terephthalate (PTT). PTT is a replacement chemical for PET and nylon, two common polymers used to make a wide range of consumer products, with several enhanced properties.

According to DuPont Tate&Lyle's website, "Susterra™ propanediol provides low toxicity and biodegradability to applications such as deicing fluids, anti-freeze and heat transfer fluids. In deicing applications, it significantly reduces energy use and emissions over other propylene glycol formulations. Susterra™ propanediol is also a key ingredient for DuPont™ Sorona® polymer and DuPont™ Cerenol™ polyols." Sorona® is a polymer used in apparel, built-in stain protection carpet, and thermoplastic elastomers used in an array of functional applications for the automotive industry. Cerenol™ is used in a variety of market applications, including personal care products, functional fluids, and specialty polymers. Examples of applications for Zemea™ propanediol include cosmetics and personal care products, as well as liquid detergents.

DuPont Tate&Lyle also claim that their Bio-PDO process consumes 40% less energy and reduces greenhouse gas emissions by 20% compared to petroleum based PDO.

## 7. Sorbitol / Isosorbide

Producing sorbitol from corn syrup is a well established industry, and at times the industry has been characterized as having excess capacity. In 2006, the production of sorbitol was dominated by four companies, producing approximately 1.2 billion pounds per year (CRADA 223 Report). Major sorbitol players include Roquette, ADM, Cerestar/Cargill, and SPI Polyol. Yet, while the production of sorbitol is well established, new production technologies are emerging to produce new chemical derivatives from sorbitol, such as isosorbide. Isosorbide is a new biochemical intermediate which can be used to produce new polymers, solvents, and plasticizers with unique properties. When isosorbide is added to PET, it makes the co-polymer stronger and more rigid. This would allow manufacturers to use less material to

manufacture their products while maintaining product strength and durability. Another unique property that isosorbide can add to the traditional PET market is increased heat tolerance, making it uniquely positioned for use in hot-fill container applications.

Several companies and research institutions, including Roquette (the world's leading producer of sorbitol) and a consortium comprising of PNNL, the Iowa Corn Promotions Board, the New Jersey Institute of Technology, and General Electric Global Research, have been developing cost effective ways to produce isosorbide from sorbitol. In June of 2008, Roquette launched their 100 MT/yr demonstration plant for the production of isosorbide diesters (POLYSORB ID®) in Lestrem, France.

Additionally, PNNL is trying to develop a more environmentally benign sorbitol production process that would not use mineral acid catalysts, which create separation and waste disposal issues. On another front, PNNL is working to develop a cost efficient production process to produce propylene glycol from sorbitol. Propylene glycol is a commonly used chemical with a wide range of product applications. Yet, it can also be derived from glycerin, a relatively low value by-product of biodiesel production.

## 8. Succinic Acid

Succinic acid is a building block chemical that can be used to produce many other commodity and specialty chemicals used in a wide array of product applications, including solvents, coatings, adhesives, plastics, fibers, lubricating oils, diesel fuel oxygenates, personal care products and cosmetics. In addition to the many market applications for which succinic acid and its derivative chemicals can be applied, another promising attribute is that its production requires CO<sub>2</sub>, leading to what some claim to be as a carbon negative process. Its potential has been recognized by many countries and was identified by the DOE in 2004 as one of the top 12 chemicals from biomass sugars and syngas. Furthermore, this chemical can be used to produce other top 12 chemicals.

While succinic acid is currently commercially produced via petrochemical production routes in small quantities (15,000 MT/yr – 50,000 MT/yr), commercially viable biobased production routes are currently being pursued by numerous companies and research institutions. The three leading companies/partnerships currently pursuing the commercialization of succinic acid are Bioamber (DNP Green Technology and Agro Industrie Recherches et Développments), Roquette and DSM, and BioEnergy International (now Myriant Technologies).

Biobased succinic acid is produced by converting the glucose and/or five carbon sugars from a variety of possible feedstocks, including corn, using a specific succinic acid fermenting microorganism and CO<sub>2</sub>. If a technology is developed and proven at commercial scale to produce biobased succinic acid that is cost competitive with similarly functioning petrochemicals, the potential world market for this four carbon

dicarboxylic acid is in excess of \$1 billion per year. And, by one account, Bioamber expects to see commercial biobased succinic acid production being reached in 2011/2012.

## IV. Top 8 Corn Products/Technologies

Upon further analysis, the top 20 list was refined down to the top 8 considered to have the greatest potential to add significant value to Minnesota's corn commodity production. This analysis was based on information gathered from more in-depth desk research and interviews with general experts within the field of biobased product and technologies and with product/technology specific representatives.

This section reviews the top 8 products and technologies, which are listed in Table 8, in more detail than was presented in the previous section.

**Table 8: Top 8 Corn Products and Technologies**

Product/Technology Name	Product/Technology Timeframe
Anaerobic Digestion	Medium
Butanol	Medium
Cellulosic Ethanol - Biochemical Platform	Medium-Long
Ethanol Distillation	Medium
Front-End Fractionation	Short
3-Hydroxypropionic Acid	Long
Succinic Acid	Medium
Zein Extraction	Medium

Short term: 0-3 years

Medium term: 3-5 years

Long term: > 5 years

### A. Anaerobic Digestion

#### 1. Product/Technology Overview

Anaerobic digestion uses bacteria to convert the thin or whole stillage by-product of ethanol production into biogas – a mixture of methane (50-80%), CO<sub>2</sub> (20-50%), and trace amounts of H<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>S, which can be burned for energy as a substitute for natural gas. This process reduces energy costs and greenhouse gas emissions and helps to conserve water relative to traditional corn-to-ethanol production. Furthermore, if collected, the struvite, a sludge that builds up in the digester, could be sold as a valuable fertilizer or a livestock feed additive, as it is composed of magnesium, phosphate, and ammonia. Additionally, if the final rulemaking for the Renewable Fuel Standard established under the Energy Independence and Security Act of 2007 (only the proposed rulemaking has been issued as of the writing of this report) continues to conclude that the greenhouse gas savings from ethanol relative to gasoline is less than the 20% threshold that the Act requires for new facilities, anaerobic digestion will provide a mechanism for an ethanol facility to reduce the greenhouse gas “score” associated with its ethanol output. However, these benefits

should be weighed against a possible reduction in revenues from the co-product sales of distillers grains, depending on whether whole or thin stillage is utilized.

There are essentially three ways in which an ethanol plant can turn their distillers grains into fuel: direct burning, gasification, or anaerobic digestion. Direct burning of the distillers grains is the simplest of these three options, but in this case, the ethanol facility sacrifices the value of the distillers grains and net energy benefits are weakened by the fact that energy is used in the process. The second, gasification, is a rather promising technology receiving a lot of recent attention; however, this technology is the least developed of the three. The third, anaerobic digestion, can use either thin or whole stillage to generate energy, requires relatively little energy to operate, and the base technology is ready now (i.e., it is already used in other industries).

Anaerobic digestion is considered an “off-the-shelf” technology because it has been around for awhile. It is currently used in many food and ag-processing industries, such as the brewery industry and for municipal wastewater treatment. However, currently, it is not widely used by the ethanol industry at any significant scale.

Anaerobic digestion refers to a decomposition process that occurs regularly in nature and that can be recreated using “digesters” or airtight tanks/ponds, where a variety of microorganisms are utilized to turn the organic material into biogas. One set of microorganisms converts the organic material to a form that another set of microorganisms can utilize in order to form organic acids that can then be utilized to produce biogas using anaerobic bacteria in an environment absent of oxygen. For every percent of methane in the resulting biogas, 10 BTUs of heat energy can be produced when the biogas is burned. One of the key factors that impacts productivity rates is temperature. While anaerobic bacteria can endure temperatures below freezing to above 135°F, they thrive best under mesophilic (98°F) and thermophilic (130°F) conditions, preferring the thermophilic range. However, processes operated in the mesophilic range are less sensitive to changes in feed materials or temperatures. Yet, due to longer decomposition time requirements, these processes also require larger digesters.

According to an August 2008 article in *Technology Review*, University of Minnesota research fellow Douglas Tiffany says that the challenge with anaerobic digesters is the expertise required to maintain a stable bacterial community at high temperatures and avoid system crashes. Additionally, capital cost requirements are not insignificant. Yet, despite its drawbacks, its potential has spurred the interest of several large companies and research universities, and research and development efforts to improve the anaerobic digestion process of corn ethanol thin and whole stillage are ongoing.

## 2. Market Potential

It is estimated that anaerobic digestion using thin stillage can reduce the energy needs of an ethanol facility by 43-66%, and if using whole stillage, energy needs could be entirely met by the biogas.

According to a study conducted by Rein and Associates, funded by AURI, anaerobic digestion could add as much as \$10 million to the bottom line of a 50 mmgy ethanol plant (2008). The study reported that if whole stillage is used, the digester could generate enough biogas to replace all the plant's natural gas needs, but that using thin stillage may be more attractive to ethanol producers because it allows for the maintained production of distillers grains (minus the solubles). According to the study, if using thin stillage, a 50 mmgy ethanol plant could produce enough biogas to displace approximately 2/3 of the plant's natural gas needs. The economics of this trade-off between using thin and whole stillage will depend on the value of distillers grains versus the cost of natural gas.

Dr. Largus Angenent and his team at Washington University<sup>13</sup> have developed an anaerobic digestion system, and he estimates that if the production rates were scaled up to industrial levels, the process could reduce the power needs of an ethanol plant by 50%.

In a February 2008 article published in the journal *Water Environment Research*, the results of a study evaluating anaerobic digestion of corn ethanol thin stillage at thermophilic temperatures in stirred tank reactors were published. The results indicated that anaerobic digestion could reduce an ethanol facility's natural gas consumption by 43-59%.

According to Otter Tail Ag Enterprises' CEO Kelly Longin, the up-front costs of the technology would be at least \$20 million for their 55 mmgy dry-mill ethanol facility (2008 AURI article).

## 3. Profiles - Companies & Research Institutions

- ♦ **POET** - POET recently began using an anaerobic digester at its cellulosic ethanol pilot plant in Scotland, SD, which uses corn cobs as its primary feedstock, producing approximately 20,000 gallons per year. The anaerobic digester is being used to power the cellulosic plant and offset natural gas usage at its attached grain ethanol plant. The intention is that once this process has been refined, it will be installed in their 25 mmgy cellulosic ethanol demonstration facility (Project LIBERTY) at Emmetsburg, IA, which is on schedule to begin production in 2011 (6/17/09, Poet press release).

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<sup>13</sup> Dr. Angenent has recently become an assistant professor of Biological and Environmental Engineering at Cornell University.

- ♦ **BioGasol** - Denmark based BioGasol is a cellulosic ethanol developer that is incorporating the use of an anaerobic digester. According to a March 2009 article in *Ethanol Producer Magazine*, BioGasol has received \$13.4 million from the Danish Energy Agency's Energy Technology Development and Demonstration Program to fund the \$45 million project of building a 1.3 mmgy cellulosic ethanol demonstration facility in Aakirkeby, Denmark. Additionally, in the U.S., the company is collaborating with Pacific Ethanol and the Joint BioEnergy Institute to build a demonstration scale plant in Boardman, OR, for which it received \$24 million from the DOE in January of 2008. According to this March 2009 article, the company intends to have this U.S. plant completed by the fourth quarter of 2009.
- ♦ **Washington University** - Dr. Largus Angenent and his team at Washington University have developed an anaerobic digestion technology that uses bacteria and cobalt to break down the thin stillage. Their research found that adding cobalt increased process yields. Dr. Angenent estimates that if the production rates were scaled up to industrial levels, the process could reduce the power needs of an ethanol plant by 50%.
- ♦ **Richard Kohn** - A patent application is currently filed for the "Process for rapid anaerobic digestion of biomass using microbes and the production of biofuels therefrom", with Richard Allen Kohn listed as the inventor. According to the patent application, it is claimed that this process is at least twice as fast as conventional anaerobic digestion processes.
- ♦ **Eisenmann AG**. – Eisenmann AG has a patent-pending anaerobic digestion process called EtOH-TS that can produce biogas and a clean effluent that can be recycled back into the fermentation process from thin stillage. According to a June 2009 article in *Biomass Magazine*, the process can produce as much as 24 million BTU/hr of biogas in a 50 mmgy ethanol facility producing 80 gal/min. Eisenmann has developed a specialized ammonia adapted microorganism to be used in an anaerobic digester so that ammonia, a product ethanol producers already have on hand, can be used as a pH neutralizer. The ammonia can then be recycled and reused to provide nutrition for the yeast during fermentation.
- ♦ **Kawartha Ethanol** – Canadian ethanol producer Kawartha Ethanol has announced plans to install an anaerobic digester in their recently completed 21 mmgy ethanol facility in Ontario, Canada.

#### 4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to anaerobic digestion technology development for the Minnesota corn industry.



**Table 9: SWOT – Anaerobic Digestion**

<p style="text-align: center;"><b><u>Strengths</u></b></p> <ul style="list-style-type: none"> <li>▪ Large market potential             <ul style="list-style-type: none"> <li>○ Size of ethanol industry</li> <li>○ Strong potential impact on ethanol margins</li> </ul> </li> <li>▪ Well established technology</li> <li>▪ Moderate institutional support</li> <li>▪ Can reduce the energy needs of an ethanol facility by 43-66%</li> <li>▪ Reduces greenhouse gas emissions</li> <li>▪ Under the RFS, as amended in 2007, this technology would help new or expanding ethanol facilities meet greenhouse gas reduction requirements.</li> </ul>	<p style="text-align: center;"><b><u>Weaknesses</u></b></p> <ul style="list-style-type: none"> <li>▪ High capital costs</li> <li>▪ Well established technology leaves marginal room for process improvement.</li> <li>▪ Potential reduction in distillers grains revenues</li> <li>▪ Cost advantage is reliant on natural gas prices.</li> <li>▪ Not yet proven at commercial scale - currently being tested in several commercial and demonstration scale facilities.</li> <li>▪ Expertise is required to maintain a stable bacterial community at high temperatures and avoid system crashes.</li> </ul>
<p style="text-align: center;"><b><u>Opportunities</u></b></p> <ul style="list-style-type: none"> <li>▪ High energy prices</li> <li>▪ A cap and trade system would further improve process economics relative to the traditional ethanol facility.</li> <li>▪ Technology offers a potential advantage for existing ethanol producers – helps keep already existing infrastructure investments profitable.</li> <li>▪ Could help ethanol utilization in California relative to other traditional Midwestern ethanol plants once the Low Carbon Fuel Standard goes into effect in 2011.</li> <li>▪ Could help provide an alternative use of distillers grains, particularly as distillers grains markets become saturated.</li> <li>▪ If the EPA grants an allowance for an ethanol blending rate of up to 15%, this will facilitate an increase in ethanol production.</li> </ul>	<p style="text-align: center;"><b><u>Threats</u></b></p> <ul style="list-style-type: none"> <li>▪ Low energy prices</li> <li>▪ High distillers grains prices</li> <li>▪ Tight capital markets</li> <li>▪ If the EPA does not grant an allowance for an ethanol blending rate of up to 15%, ethanol production volumes will be constrained by the current 10% “blend wall”</li> </ul>

## B. Butanol

### 1. Product/Technology Overview

Butanol is a 4 carbon alcohol. Other chemical compounds in the alcohol family include methanol (1 carbon), ethanol (2 carbon), and propanol (3 carbon). It is currently produced mainly via petrochemical feedstocks and is used primarily as an industrial solvent. Yet, if proven commercially cost competitive, butanol could also be produced via sugar fermentation and could function as an alternative renewable fuel. Table 10 lists the derivative chemicals that can be produced from butanol, their applications, and the institutions/companies involved in its development.

**Table 10: Butanol – Derivatives, Applications, and Institutions/Companies Involved**

Derivatives <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/Companies Involved <sup>1</sup>
<ul style="list-style-type: none"> <li>– Butyl Acrylate</li> <li>– Methacrylate</li> <li>– Glycol Ethers</li> <li>– Butyl Acetate</li> </ul>	<ul style="list-style-type: none"> <li>– -Fuel</li> <li>– Solvents</li> <li>– Coatings - paint, varnish, and inks</li> <li>– Agricultural chemicals insecticides and herbicides</li> <li>– Synthetic resins and adhesives</li> <li>– Textiles (e.g., scatter rugs, bathmats)</li> <li>– Sealants</li> </ul>	<ul style="list-style-type: none"> <li>– BP and DuPont</li> <li>– ButylFuel LLC</li> <li>– TetraVita BioScience</li> <li>– Gevo</li> <li>– Cobalt Biofuels</li> <li>– Green Biologics</li> <li>– Syntec</li> <li>– METabolic Explorer</li> <li>– University of Illinois</li> <li>– University of California</li> <li>– Caltech</li> <li>– Ohio State University Research Foundation</li> <li>– Joint BioEnergy Institute</li> <li>– USDA, ARS</li> </ul>

Source: Informa Economics

1/ Not an exhaustive list

While butanol has traditionally been produced via petrochemical routes, the technology to produce biobutanol from non-petrochemical feedstocks such as corn has been around for several decades. It has just not been cost competitive. The most common process for producing biobutanol in the past has been acetone-butanol-ethanol (ABE) fermentation, using *Clostridium acetobutylicum* as the fermenting bacterium. This process was common during World War II, but was phased out as petrochemical routes became more economical. Then, as the interest in renewable fuel production gained momentum, biobutanol once again entered into the discussion. Yet, despite its many benefits over ethanol, which include a higher energy content and the ability to transport it in existing pipelines, low yield and low concentrations prevented it from being economically competitive, and the ethanol market took off.

“Traditional” ABE fermentation yielded butanol, acetone, and ethanol at a ratio of 6:3:1. One bushel of corn would produce 1.3 gallons of butanol, 0.7 gallons of acetone and 0.13 gallons of ethanol. This 1.3 gallons per bushel was much lower than the ethanol production process that then produced 2.5 gallons per bushel. According to David Ramey of ButylFuel, other limitations of the “traditional” ABE fermentation process include:

- ♦ Toxicity - At alcohol concentrations of 1-2%, the fermenting bacteria are killed.
- ♦ Low final concentration - 1-2%, relative to 10-15% for ethanol.
- ♦ A high boiling point of 117°C, and at the 1-2% final batch concentration, there is a lot of water to boil off.

However, over the past 20 years, research and development efforts have focused on improving various aspects of the ABE process. Molecular biology research has focused on developing various microbial strains with improved tolerance to butanol toxicity, which has resulted in significant yield increases. In 1990, the bacterium *Clostridium beijerinckii* was developed by Hans Blaschek from the University of Illinois, doubling butanol production over its parent strain, *Clostridium acetobutylicum*. Additionally, the development and application of in-situ gas stripping to remove the solvent from the fermenter, which minimizes product inhibition (the problem whereby the butanol becomes toxic to the fermenting agent), has enabled much higher feed concentrations. With this process, butanol, acetone, and ethanol production in a fed-batch mode reached a ratio of 65:35:1 (Argonne National Laboratory), a drastic improvement over the 6:3:1 ratio yielded via “traditional” ABE fermentation methods. A yield of 2.5 gallons of butanol and little to no acetone and ethanol per bushel of corn is now commonly reported.

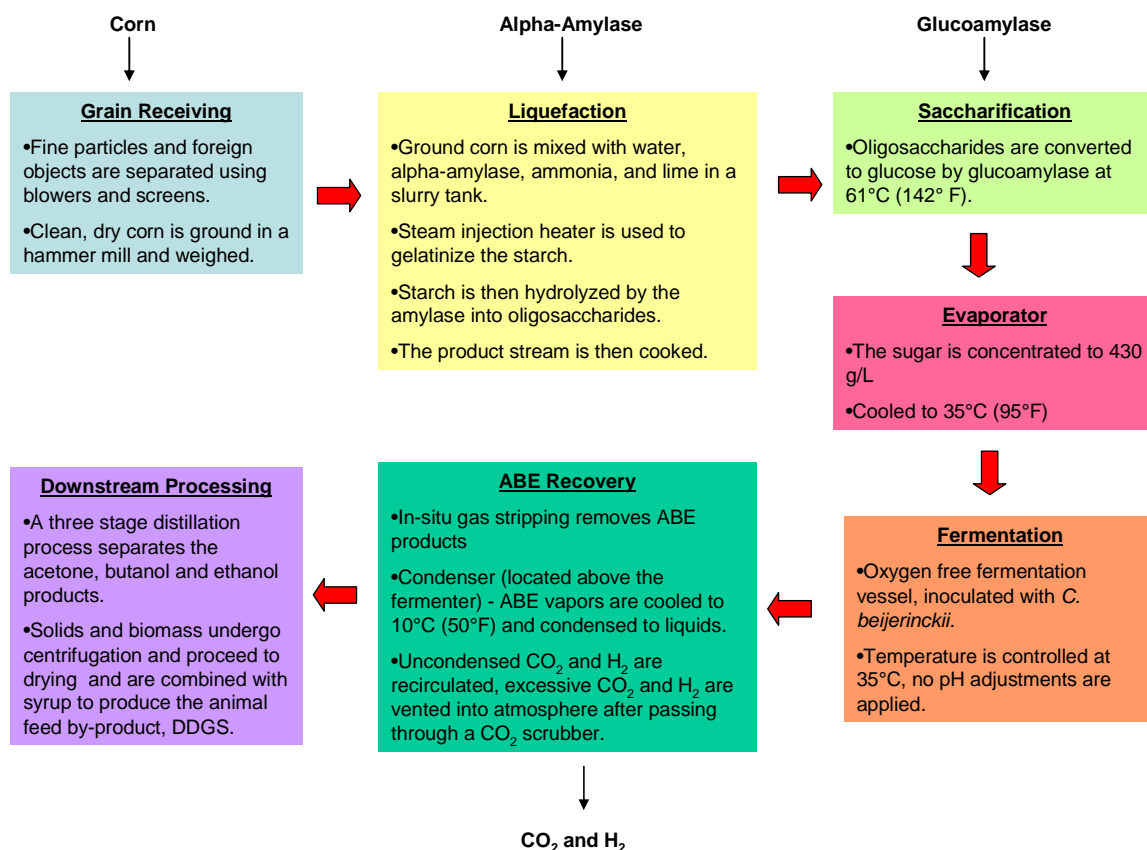
The following is a description of the ABE fermentation process developed by Qureshi and Blaschek (from 1999 and 2001 studies) and reported within the Argonne National Laboratory November 2007 report, “The Life-Cycle Assessment of Corn-Based Butanol as a Potential Transportation Fuel”. In this process, acetone, butanol and ethanol are produced from the bacterium *Clostridium beijerinckii*. The description and visual illustration (Figure 18) below serve as a basis for understanding the biobutanol production process. However, there are many variations on this theme and other production technologies are being developed by various companies and research institutions, many of which will be profiled in section IV.B.3, “Profiles - Companies & Research Institutions”.

*“Corn is fed into a conventional corn dry mill for conversion to glucose through liquefaction and saccharification. The glucose is fermented to ABE through a fed-batch system. After fermentation, the ABE compounds are removed by means of in-situ gas stripping. ABE products are recovered through molecular sieve adsorption and a three-stage distillation that separates the acetone, butanol, and ethanol. Solids and biomass that are removed from grain processing and fermentation undergo centrifugation and proceed to drying,*

*along with syrup from distillation; DDGS generated from drying is used as animal feed."*

(Argonne National Laboratories)

**Figure 18: ABE Fermentation Process**



Source: Argonne National Laboratory and Informa Economics

It was noted in the text of the Argonne National Laboratory report that condensing the sugars to 430g/L (refer to the evaporator step in Figure 18) is a concentration eight times higher than that required in ethanol production, and that while there are alternative technologies available, this step requires a large amount of heat and additional capital for the necessary equipment.

## 2. Market Potential

In 2007, the worldwide butanol market was estimated at about 350 mmgy, with the U.S. accounting for 220 mmgy (*Ethanol Today*, March 2007). According to a September 2008 presentation by Cobalt Biofuels, the worldwide chemical butanol market is estimated at \$864 million. By February 2009, the price of butanol had reached \$3.64-\$3.92 per gallon (ICIS).

If butanol were to become cost competitive in the fuel market, the market potential becomes much larger, likely several billion gallons. Butanol possesses many positive properties that make it worthy of consideration as a potential biofuel. Benefits include:

- ♦ High energy content – the energy content of butanol is 99,840 BTU per gallon – 86% of gasoline and 30% higher than ethanol. (Argonne National Laboratory, Nov. 2007)
- ♦ Low water solubility (not as hydroscopic as ethanol) – reduces corrosion in fuel tanks and pipelines, enabling butanol to be stored and transported via traditional petroleum infrastructure, as opposed to ethanol which cannot be transported through existing pipelines.
- ♦ Less evaporative than both gasoline and ethanol – it is safer to use and generates fewer volatile organic compound emissions.
  - Low Reid Vapor Pressure (RVP) - the RVP of butanol is 0.33 pounds per square inch (psi) versus ethanol's 2 psi and gasoline's 4.5 psi. This makes butanol 6 times less evaporative than ethanol and 13.5 times less than gasoline.
- ♦ Can be blended at higher concentrations.
  - Currently, biobutanol can be blended up to 10% by volume in European gasoline and 11.5% in U.S.
  - With the results of recent trials, there is potential to increase this to 15-16%.
  - Some studies have shown that butanol can even be used between 85-100% without the need for any engine modification. However, at this level, fuel mileage is compromised relative to gasoline.
- ♦ Can be produced from the same feedstocks as ethanol (e.g., corn, wheat, sugar beet and sugar cane).
- ♦ The production process is similar to ethanol, allowing for the possibility of retrofitting existing ethanol facilities.
- ♦ Can be upgraded to higher valued molecules for use in a wide array of industrial applications. This four carbon building block chemical can be used to make gasoline, diesel, or jet fuel using traditional refinery reactions.
- ♦ Can benefit from many of the same technologies as those being developed for cellulosic ethanol.
- ♦ Blending butanol with ethanol allows for higher ethanol usage.
- ♦ Relatively low carbon footprint – A 2007 study, "Life-Cycle Assessment of Corn-Based Butanol as a Potential Transportation Fuel", conducted by Argonne National Laboratory concluded that the production of corn-based butanol achieves energy benefits and reduces greenhouse gas emissions, but that the results varied depending on the method used to treat the co-product acetone<sup>14</sup>.

<sup>14</sup> According to a February 2008 press release, BP and DuPont have commissioned a full environmental life cycle analysis of their proposed biobutanol process.

### 3. Profiles - Companies & Research Institutions

Many of the companies currently pursuing biobutanol production are planning on first marketing their product to the chemical solvent market and later into the fuel market. As biobutanol production grows, the current premium price will be reduced to commodity levels. While these industrial applications of butanol give new biobutanol market entrants a high-valued product outlet, its growth potential in this market is limited. In order for biobutanol to grow beyond the current market estimate of 350 mmgy, it must eventually be competitive in the fuel market.

The discussion thus far has focused on the general term butanol (or biobutanol if specifically noting that it was produced from non-petrochemical feedstocks), which typically refers to the straight chain butanol isomer, n-butanol. However, there are companies pursuing the development of other butanol isomers, which include sec-butanol, iso-butanol, and terc-butanol. According to Gevo, a company currently pursuing the development of isobutanol, the key production process difference between the various isomers is the fermenting agent itself. As a fuel, Gevo states that isobutanol has a higher octane level than n-butanol but is similar to n-butanol in other performance characteristics such as RVP and water solubility. Additionally, the company states that since you are starting out with a longer chain alcohol, it is “easier/simpler” to then derive higher valued fuel products that target jet and diesel fuel markets.

In general, it is assumed that unless otherwise stated, the companies/institutions profiled below are referring to the standard, straight chain isomer, n-butanol. However, many companies do not specify and could be using the generic term “butanol” to refer to any of the four isomers, as the terminology is not consistent within the industry.

#### **BP and DuPont (also working with British Sugar)**

- ♦ DuPont scientists have genetically modified *E.coli* to make butanol. The company is now looking to extend the technology to make the butanol isomers 2-butanol and 2-methylpropanol (isobutanol). These other butanol isomers differ from butanol in their chemical structures and they have somewhat different melting and boiling points. Nonetheless, they are all less hydroscopic than ethanol and more so than longer carbon chain alcohols.
- ♦ A \$400 million demonstration facility in the UK is expected to begin producing 5 mmgy in 2010. They are then expecting to have their first commercial plant operational by 2013.
- ♦ BP and DuPont have commissioned a full environmental life cycle analysis of their proposed biobutanol process, according to a February 2008 BP press release.
- ♦ Recently (July 2009), BP and DuPont announced the commencement of their butanol commercialization venture, Butamax Advanced Biofuels. Butamax, based out of Wilmington, Delaware, will complete the ongoing biobutanol research and development program and eventually expects to license the



technology to other biofuel producers as well as work with fuel blenders and distributors to bring biobutanol to the global fuel market.

### **ButylFuel LLC**

- ♦ ButylFuel, LLC (formerly Environmental Energy Inc.) has developed a patented process which it claims makes butanol production more economically viable and competitive with current petrochemical processes and with the production of ethanol.
- ♦ Process improvements made under a federal Department of Energy Small Business Technology Transfer (DOE/STTR) grant include:
  - A recovery process whereby the solvents are continuously removed. This essentially prevents alcohol accumulation to levels that are lethal to the fermenting microbe.
  - A gravity driven process, whereby the costly recovery problem associated with the high boiling point is resolved.
  - A continuous process which eliminates the need to clean up every 4-5 days and having to restart the fermentation, thus reducing associated costs.
- ♦ The process produces 2.5 gallons of butanol per bushel of corn with no acetone or ethanol. Also, it produces hydrogen as a by-product.
- ♦ Preliminary cost estimates suggest that their biobutanol production process produces butanol at costs much lower than that of petro-butanol and slightly less than ethanol.
  - Cost estimates suggest that they can produce biobutanol at \$1.20 per gallon (not including a credit for the hydrogen), compared to \$1.28/gal for ethanol with gasoline at \$1.35/gal and corn at \$2.50/bu. Another way to view this is the energy that is produced per dollar - 105,000 BTU/\$ for butanol versus 84,000 BTU/\$ for ethanol.
  - While these prices are somewhat dated given commodity market developments over the last few years, they may still be indicative of relative prices among commodities.
- ♦ ButylFuel is currently completing testing at their 50 gal/week pilot plant, and is working on designs of a 1,000 gal/week demonstration plant.
- ♦ ButylFuel expects commercialization to be reached in one year.
- ♦ According to an interview with a ButylFuel founder and technical director, David Ramey, their competitive advantage relative to their competition is that “we have a higher yield ~2x with about 42% more energy out with Bu100 (100% biobutanol) production, we are less expensive to produce and recover and we are continuous.” Additionally, the representative pointed out that some of its competitors will have “to overcome the stigma of genetically modified organisms such as e-coli...”
- ♦ In terms of current barriers/hurdles/threats to their commercialization process and to butanol in general, Ramey responded that the company had resolved all problems associated with the production and recovery of biobutanol, but that acceptance, governmental testing, and funding were current barriers.



### **TetraVitae BioScience**

- ♦ TetraVitae BioScience has patented a mutant strain of *Clostridium beijerinckii*, developed by company co-founder Hans Blaschek from the University of Illinois that produces higher butanol yields. TetraVitae BioScience claims that their bacterium is more genetically stable, robust, and responsive to genetic modification and improvement, than previous strains.
- ♦ The process results in high final product concentration and reduced product inhibition.
- ♦ The company is currently enhancing strains, developing more efficient process engineering, and looking for the ability to use low-cost feedstocks.
- ♦ TetraVitae is currently working on scaling up their biobutanol production process. They are currently producing biobutanol in a 300 liter reactor.

### **University of Illinois, Hans Blaschek**

- ♦ Recent research has focused on producing a second generation of the strain.
- ♦ Dr. Blaschek's work has funding from the Department of Energy, Illinois Corn Marketing Board, Illinois-Missouri Biotechnology Alliance, Council for Food and Agricultural Research, Mitsubishi Chemical and the USDA Value-Added Non-Foods program.
- ♦ According to Dr. Blaschek, distillation is one of the largest differences between ethanol and butanol production, as it is currently a very energy intensive process. However, Blaschek points out that there are a lot of people working on this issue and believes the issue can be solved within the next two years.
- ♦ Dr. Blaschek says that sensitivity analysis suggests that biobutanol will be economically competitive at crude oil prices around \$60/bbl.
- ♦ Dr. Blaschek believes that TetraVitae's biobutanol production process will be commercialized within the next two years.
- ♦ Current barriers to commercialization include scaling up the production process and all the "unique issues" that that entails.

### **Gevo**

- ♦ Gevo has developed a process known as "Gevo's Integrated Fermentation Technology" (GIFT). GIFT enables the production of isobutanol and hydrocarbons from retrofitted ethanol plants. No acetone or ethanol is produced. They are planning to focus initially on isobutanol development and then later add on a hydrocarbon component and cellulosic, fractionation and biorefinery concepts.
- ♦ The company was founded in 2005 by Drs. Frances Arnold, Matthew Peters and Peter Meinhold of the California Institute of Technology.
- ♦ In December 2007, Gevo acquired an exclusive license for the method developed by Dr. James Liao at the University of California, Los Angeles (UCLA) for modifying the metabolic pathway of *E.coli* bacteria for the non-fermentative synthesis of higher alcohols.
  - Liao was quoted in January of 2008 as saying, "We should be in the initial stages of commercial scale biobutanol production in two to three years."

- ♦ In May 2008, it closed a \$17 million third round of financing to add to the \$30 million it had already raised since January, 2007.
  - Gevo is backed by venture capitalists Richard Branson (Virgin Green Fund), Vinod Khosla (Khosla Ventures), Burrill and Company, the Malaysian Life Sciences Capital Fund and Total.
- ♦ In November of 2008, Gevo entered into an exclusive partnership with the engineering and construction firm ICM to commercialize the technology.
- ♦ Gevo also has a joint agreement with Bye Energy to explore opportunities for the marketing and distribution of renewable aviation fuels to small and medium sized airports.
- ♦ Gevo claims that GIFT yields economic concentrations and a simple, inexpensive way to separate butanol from water, a current challenge to biobutanol production technology development.
- ♦ The isobutanol process unit would cost about \$30 million to retrofit an existing 100 mmgy ethanol facility. Then, to add on the hydrocarbon unit it would cost an additional \$18 million.
- ♦ Production costs are expected to be 50% of the cost of petrochemical based butanol production processes (assuming February 2009 oil prices).
- ♦ Gevo is now operating a 10,000 gal/yr pilot plant.
- ♦ The company expects to be operating at 1 mmgy by the end of August 2009 at ICM's St. Joseph, MO, biofuels research center, by retrofitting an existing ethanol facility.
- ♦ Gevo then expects to have its first commercial scale plant on-line, producing 20-50 mmgy of isobutanol and other hydrocarbons by 2011.

#### Caltech, Frances Arnold

- ♦ Frances Arnold, co-founder of Gevo and professor at Caltech, is currently working on developing cellulases (an array of enzymes) that can metabolize cellulose and create fuel in one step.

#### **Cobalt Biofuels**

- ♦ Cobalt Biofuels has made advances in microbial strain fermentation reaction management and separation technology.
  - This fermentation reaction management technology allows their continuous fermentation process to operate at peak production rates for extended periods of time.
  - They have patented a vapor compression distillation (VCD) fluid separation technology that removes alcohol from the fermentation vessel using 25-50% of the energy required by typical separation techniques. The water used by the VCD process is then recycled.
  - The company is now developing and patenting a high-throughput process to identify the optimal microbe for any selected feedstock. They are also engineering a bioreactor where biomass enters the bioreactor, the bacteria processes this biomass, and butanol and water flow out.
- ♦ Cobalt had raised a total of \$38 million to accelerate the commercialization of their biobutanol production process as of September 2008. Investors include

Pinnacle Ventures LLC, Vantage Point Venture Partners, The Malaysian Life Sciences Capital Fund, @Ventures, LSP, and Harris and Harris.

- ♦ They expect to build a 35,000 gal/yr pilot plant in 2009, a 2.5 mmgy demonstration scale plant in 2010, and a commercial scale facility producing 25 mmgy in 2012.
- ♦ Pamela Contag, company founder and CEO, says, “Our models tell us it is a very low-cost process that can be competitive with anything on the market today” (October 2008).

#### **Green Biologics / EKB Technology**

- ♦ Green Biologics is based in Oxfordshire, UK, and is working with EKB Technology.
- ♦ The company has developed their own heat-tolerant thermophilic bacteria and thermostable enzymes for producing biobutanol from biomass.
- ♦ Their technology can be used to retrofit existing commercial scale ethanol facilities.
- ♦ Their process produces higher yields and is tolerant to butanol concentrations up to 4%.
- ♦ The goal is to achieve a two-to-three fold increase in butanol yield and a two-to-three fold decrease in cost.
- ♦ In 2008, they installed a 300 liter/yr lab scale operation at their Milton Park headquarters.
- ♦ The company is currently working with existing biobutanol producers to incorporate their technology into existing facilities. They have signed a letter of intent for a strategic partnership with a Chinese biobutanol producer and plan to build a 1,000 metric ton/yr demonstration scale facility in India with biochemical partner, Laxmi Organic Industries. The goal is to have the plant fully operational in 2010. This particular plant will run on molasses produced from the sugarcane industry.

#### **METabolic EXplorer**

- ♦ METabolic Explorer is based in Clermont-Ferrand, France.
- ♦ The company is using their expertise in molecular biology, metabolic engineering and bioinformatics to design high-performance microorganisms to transform plant material to existing bulk chemicals, including butanol.

#### **Agriculture Research Service (ARS), USDA**

- ♦ The ARS is in the process of refining an integrated method for producing cellulosic biobutanol that could make biobutanol more competitive with ethanol and gasoline.
- ♦ Key researchers include: Nasib Qureshi, Bruce Dien, Michael Cotta, and Badal Saha.
- ♦ They have consolidated three of the four steps into a simultaneous saccharification, fermentation and recovery process using wheat straw as a feedstock. After the wheat straw has been pretreated with dilute sulfuric acid or other chemicals, the material is fermented in a bioreactor containing different

types of enzymes and the *C.beijerinckii* bacteria. These enzymes and bacteria do their jobs simultaneously. Throughout this process, gas stripping is used to remove the acetone, butanol and ethanol as they are produced.

- ♦ Early trials showed a two fold increase in productivity above traditional glucose-based fermentation, but the pace of fermentation outran the pace of hydrolysis and they changed to fed batch system.
- ♦ The process, if scaled up, could produce 99 gallons of alcohol per ton of wheat straw. In comparison, Dr. Richard Bain at NREL says the current expected yields for cellulosic ethanol from a biochemical process is about 90 gal/ton of biomass. Dry-mill corn ethanol yields about 102 gal/ton of grain.
- ♦ Currently, they are using a strain of *C.beijerinckii* which produces acetone butanol and ethanol, but efforts are underway to develop a bacterium to produce only butanol.

#### **Joint BioEnergy Institute (JBEI)**

- ♦ The JBEI has “engineered the common industrial yeast *Saccharomyces cerevisiae* with an n-butanol biosynthetic pathway, resulting in a ten-fold improvement in n-butanol production from one of the strains to 2.5 mg/L.” (Steen et al., December 2008).
- ♦ Steen et al. point out that while *Clostridia* strains are commonly used as the fermenting agent in butanol production, *Clostridia* has several drawbacks:
  - Relative lack of genetic tools to manipulate their metabolism
  - Slow growth
  - Intolerance to n-butanol above 1-2%, and
  - Production of butyrate, acetone, and ethanol as by-products.

## **4. SWOT**

The following is a summary of the strengths, weaknesses, opportunities and threats to butanol technology development for the Minnesota corn industry.

**Table 11: SWOT – Butanol**

<p style="text-align: center;"><b><u>Strengths</u></b></p> <ul style="list-style-type: none"> <li>▪ Very large market potential</li> <li>▪ Several advantages over ethanol, including:             <ul style="list-style-type: none"> <li>○ Higher energy content</li> <li>○ Can be transported via traditional infrastructure.</li> <li>○ Can be blended with gasoline at higher blend levels.</li> <li>○ Less evaporative than both gasoline and ethanol – it is safer to use and generates fewer volatile organic compound emissions.</li> </ul> </li> <li>▪ Its development is further along than many other advanced biofuel technologies and its implementation requires less capital investment.</li> <li>▪ Appears to be cost competitive with current petrochemically produced butanol, and based on some company claims, it may be close to being competitive with ethanol.</li> <li>▪ Strong institutional support</li> </ul>	<p style="text-align: center;"><b><u>Weaknesses</u></b></p> <ul style="list-style-type: none"> <li>▪ Not yet proven at a commercial scale.</li> <li>▪ Not yet cost competitive with ethanol.</li> <li>▪ Moderate-high capital costs</li> <li>▪ Lack of access of retrofitted ethanol plants to pipeline origins</li> <li>▪ Marketing issues associated with penetrating a well established market.</li> <li>▪ Benefits from this technology are not limited to corn; other sugar feedstocks can also be utilized – will depend on regional economics.</li> </ul>
<p style="text-align: center;"><b><u>Opportunities</u></b></p> <ul style="list-style-type: none"> <li>▪ High crude oil prices</li> <li>▪ Can benefit from cellulosic ethanol technology developments.</li> <li>▪ Ability to utilize current ethanol infrastructure – current ethanol facilities can be retrofitted to produce butanol.</li> <li>▪ First mover advantage – ability to capture higher prices initially from high value, non-fuel markets.</li> <li>▪ “Green product” marketability for chemical product applications (e.g., solvents) – may command small premium in niche markets/products.</li> <li>▪ Could be used to make any type of traditional fuel using traditional refinery reactions.</li> </ul>	<p style="text-align: center;"><b><u>Threats</u></b></p> <ul style="list-style-type: none"> <li>▪ Low crude oil prices</li> <li>▪ High feedstock costs</li> <li>▪ Tight capital markets</li> <li>▪ Favorable economic competitiveness of non-corn based butanol.</li> <li>▪ If the EPA grants an allowance for an ethanol blending rate of up to 15%, this might moderately counteract the blending rate advantage for butanol.</li> </ul>

## C. Cellulosic Ethanol – Biochemical Platform

### 1. Product/Technology Overview

There are two main technology pathways being developed for the production of cellulosic ethanol from lignocellulosic feedstocks: biochemical and thermochemical. There have been significant investments made in the development of both of these production routes, and commercial scale facilities have been proposed and are beginning to be built. Yet, there are still significant research and development efforts needed for this technology to become commercially viable.

While the “winner” of these two routes is yet to be determined, Informa has chosen to focus on the biochemical platform based on information gathered from interviews and desk research. While the base technology for the thermochemical platform is more developed, its application in the world of cellulosic ethanol would reportedly require very large facilities in order to reach economies of scale. This larger scale requires feedstocks to be brought in from greater distances, which erodes economic competitiveness. Additionally, given that the biochemical approach is “newer”, there is more room for process improvements. Also, several interviewees expressed statements to the effect that the biochemical platform produces a product that can be used today, whereas the thermochemical platform produces a product that has to undergo additional processing to reach a usable product form. Furthermore, the biochemical platform allows for multiple value-added product streams to be carved out – sometimes referred to as a biorefinery concept.

In terms of the biochemical platform, research and development are focused on the high production cost areas of pretreatment, hydrolysis, and fermentation<sup>15,16</sup>. Whereas the main carbohydrate in traditional corn-to-ethanol production is starch, lignocellulosic biomass is composed of cellulose (35-50%), hemicellulose (20-35%), and lignin (10-25%)<sup>17</sup>. The cellulose is composed of glucose (a 6 carbon or hexose sugar); while the hemicellulose contains primarily xylose (a 5 carbon or pentose sugar), yet it also contains a mixture of other 5 carbon sugars such as arabinose and small amounts of glucose. One of the key challenges presented by the biochemical platform over traditional corn-to-ethanol technology is that it is far more difficult, and thus more costly, to hydrolyze cellulosic biomass than it is to hydrolyze starch, and that while hemicellulose is relatively easy to hydrolyze compared to cellulose, it is more difficult to ferment.

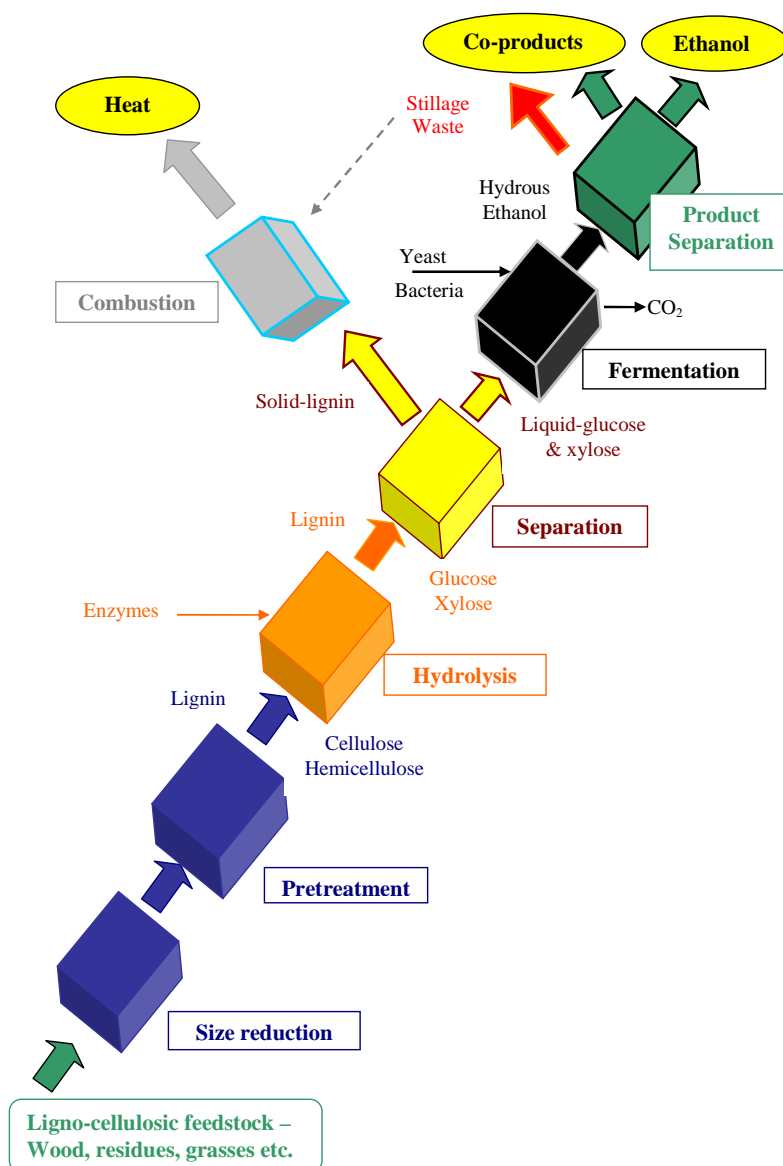
<sup>15</sup> Distillation costs are another large cost component to the overall process, and distillation and dehydration technology developments being made traditional corn-to-ethanol production processes will also apply to cellulosic ethanol processes. See section III.A.4 “Ethanol Distillation” for more details.

<sup>16</sup> Logistical costs and considerations are another large part of the overall economic viability of cellulosic ethanol production technologies. However, these issues and costs are not discussed within this study.

<sup>17</sup> Corn stover is composed of approximately 36.0% cellulose, 23.4% hemicellulose, and 18.6% lignin (Dien et al., 2006).

The following discussion outlines the general cellulosic ethanol production process currently being developed for the biochemical platform. It is also illustrated in Figure 19. However, as discussed below, there are differences between individual processes, as some of these steps can be combined. Additionally, the order along the production chain in which the lignin is separated out differs between processes. In some processes, the lignin is removed during pretreatment, in others it is removed after hydrolysis, and in others it goes along with the sugars until the end and is removed after fermentation.

**Figure 19: Cellulosic Ethanol – Biochemical Process Diagram**



Source: International Energy Agency, "From 1<sup>st</sup>-to 2<sup>nd</sup> - Generation Biofuel Technologies"



### Step 1 - Pretreatment

The pretreatment of biomass is currently one of the single largest cost components in the overall cellulosic ethanol production process via the biochemical platform, accounting for 19% of the overall cost, second only to raw material costs (NREL, May 2007 presentation). However, this step is necessary in order to open up the structure of the biomass sufficiently to allow for effective hydrolysis.

There are many pretreatment methods currently being developed by numerous companies and research institutions. At this time, there is not a clear front-runner in emerging pretreatment processes, as each process has its own benefits and disadvantages. There are physical pretreatment processes, generally involving some type of grinding, shredding or chopping, and there are chemical pretreatment processes. Chemical pretreatments can be alkalines<sup>18</sup> (e.g. sodium hydroxide, ammonia, ammonium sulfite), acids (e.g., sulfuric acid, hydrochloric acid, phosphoric acid), or even water heated to high temperatures. In general, the stronger the acid the greater the hydrolysis yield and the more fermentation inhibitors created. Whereas, the more alkaline approaches tend to result in less effective hydrolysis but fewer inhibitors are produced. According to Dien and Bothast (2007), most pretreatments encompass multiple mechanisms. And according to personal communications with Bruce Dien<sup>19</sup>, the more common approaches currently being pursued are that of dilute acid and steam explosion, or a combination thereof.

A brief description of select chemical pretreatment processes is provided in Table 12, including, but not limited to, those identified by the Consortium for Applied Fundamentals Innovation (CAFI). CAFI was formed in early 2000 to compare leading pretreatment technologies (indicated by the red text).

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<sup>18</sup> Not a viable option for woody crops, more appropriate for herbaceous crops.

<sup>19</sup> Bruce Dien is a chemical engineer in the Fermentation Biotechnology Research department of the USDA, ARS, at the National Center for Agricultural Utilization Research.

**Table 12: Chemical Pretreatment Processes**

Technology <sup>1</sup>	Description of Technology	Institutions / Companies Involved <sup>1</sup>
Dilute Acid (Sulfuric Acid)	A high pressure/temperature reactor mixes biomass and dilute acid, converting the hemicellulose to xylose and making the cellulose enzyme digestible without the need for explosive decompression. CAFI found the process to achieve a 91.1% conversion of corn stover at 72 hours for an enzyme loading of 15 filter paper unit (FPU) per gram of cellulose. This process released mostly xylose sugars. However, process limitations include: limitations in solids concentrations to about 30%, expensive construction materials due to the corrosive environment of the process, separation of the liquid hydrolyzate from the pretreated solids, acid neutralization costs, costs associated with the removal of product inhibitors produced from the process, energy costs associated with the high temperature/pressure, and yield losses during hydrolyzate conditioning. All of these limitations make this a relatively high cost process.	<ul style="list-style-type: none"> <li>- NREL</li> <li>- Netherlands Organization for Applied Scientific Research, Techno Invent, and Wageningen University and Research Centre (BioSulfurol Process)</li> <li>- University of California, Riverside - Charles Wyman</li> </ul>
Steam Explosion & Sulfur Dioxide	Steam explosion requires high pressure and high temperature, which is then suddenly reduced, causing the materials to undergo explosive decompression. Sulfur dioxide has been used in steam explosion to achieve similar yields to dilute sulfuric acid. One advantage over dilute sulfuric acid is the more rapid penetration of the sulfur dioxide and possible recyclability. However, there are safety concerns, and costs are projected to be similar to dilute sulfuric acid.	<ul style="list-style-type: none"> <li>- Lund University, Sweden</li> <li>- Iogen (modified steam explosion process)</li> <li>- University of British Columbia</li> <li>- Budapest University of Technology and Economics</li> <li>- ENEA-National Agency for New Technology, Energy, and Environment (Italy)</li> </ul>
Controlled pH	By monitoring and controlling the pH at near neutral conditions, hydrolytic reactions are minimized, while physical changes are maximized. This process helps to enhance the susceptibility of cellulose to enzymes and avoids formation of the inhibitory products which later interfere with cellulose hydrolysis or ethanol fermentation. It also helps maximize physical changes that improve enzymatic hydrolysis of cellulose, decrease cellulose crystallinity, and lowers the association of cellulose with lignin. CAFI found the process to achieve a 85.2% conversion of corn stover at 72 hours for an enzyme loading of 15 FPU/g of cellulose.	<ul style="list-style-type: none"> <li>- Purdue University - M. R. Ladisch and N. Mosier</li> <li>- USDA, ARS - B. Dien</li> </ul>

Technology <sup>1</sup>	Description of Technology	Institutions / Companies Involved <sup>1</sup>
Ammonia Fiber Expansion (AFEX)	A patented process whereby lignocellulosic material is treated with liquid ammonia under pressure and then by rapidly releasing that pressure cellulose and hemicellulose are converted to fermentable sugars at very low enzyme levels. CAFI found the process to achieve a 96.0% conversion of corn stover at 72 hours for an enzyme loading of 15 FPU/g of cellulose. An added advantage is that the ammonia is recyclable and there is no need to wash or detoxify the pretreated material, as is the case with acid pretreatments. Construction costs for the process are lower than for the dilute sulfuric acid, the hydrolyzate is compatible with fermentation organisms without conditioning, and the process does not produce inhibitory products. The AFEX process is more effective on biomass that does not contain high levels of lignin.	– Michigan State University - Bruce Dale
Fiber Extrusion (FIBEX)	Similar to AFEX, only it is a continuous process as opposed to a batch process. The added advantage is that this process reduces the time and ammonia levels required, while giving similar results.	
Ammonia Recycle Percolation (ARP)	An ammonia solution is passed through a reactor with biomass at 80°-180°C. Then, the ammonia is separated and recycled. This process fractionates the biomass into three components (pentose, cellulose, and lignin). At high temperatures, the ammonia breaks down the lignin. By removing the lignin, microbial activity and overall enzyme efficiency is increased, thus reducing enzyme requirements and costs. CAFI found the process to achieve a 90.1% conversion of corn stover at 72 hours for an enzyme loading of 15 FPU/g of cellulose. The disadvantage of this process is the challenge in reducing liquid loadings to keep energy costs low.	– Auburn University - Y.Y.Lee – Kyungwon University, Korea – Iowa State University— K. Tae Hyun
Soaking in Aqueous Ammonia (SAA)	A process being developed to reduce the liquid loading and energy costs of the ARP process.	– Auburn University – NREL – Iowa State University - K. Tae Hyun
Lime	Lime is a relatively low cost, safe to handle and available chemical that removes lignin and improves cellulose digestion by enzymes. Lime can then be recycled by using water and carbon dioxide. CAFI found the process to achieve a 93.0% conversion of corn stover at 72 hours for an enzyme loading of 15 FPU/g of cellulose. However, the process is slower than that of ammonia or other more expensive bases. Therefore, low cost pretreatment containment, such as treatment in piles, is needed in order to be cost effective.	– Texas A&M University - Mark Holtzapple
Organosolv	An organic or aqueous organic solvent is used to remove or breakdown the lignin and part of the hemicellulose, leaving reactive cellulose in the solid phase. An additional catalyst can also be used to reduce operating temperatures or to enhance the delignification process. This process does not produce inhibitory products and does not use corrosive acids which require washing/detoxing and high cost construction materials.	– Lignol Innovations, - Kendall Pye
Solvent-Based Clean Fractionation	This process uses a solvent-based pretreatment to separate/fractionate cellulose, hemicellulose, and lignin. This process allows the lignin and the hemicellulose to be used as a feedstock in higher-valued products, as opposed to other pretreatment technologies which use these products as fuel and fermentation feedstocks, respectively.	– NREL

Technology <sup>1</sup>	Description of Technology	Institutions / Companies Involved <sup>1</sup>
Cellulose Solvent-Based Lignocellulose Fractionation	Virginia Tech has developed a pretreatment process they claim to be cost effective. The process, licensed by Mascoma, uses a combination of three technologies: a cellulose solvent pretreatment, concentrated saccharification and organosolv. This process does not use corrosive chemicals, high pressure or high temperature. Products produced from this process include amorphous cellulose, hemicellulose sugars, lignin, and acetic acid. Amorphous cellulose is a form of cellulose that is more accessible to further hydrolysis and is hydrolyzed by adding a special enzyme developed by Genencor International. Results have shown a 97% conversion of corn stover cellulose after 24 hours at an enzyme loading level of 15 FPU/g of cellulose.	<ul style="list-style-type: none"> <li>– Virginia Tech - Percival Zhang</li> <li>– Dartmouth College - Lee R. Lynd</li> <li>– Mascoma</li> </ul>
Ionic Liquid	An ionic liquid solvent is used along with a co-solvent such as acetone and an anti-solvent such as ethanol and/or water to break apart the crystalline plant cell walls and loosen lignin and hemicellulose materials. Results have shown 95% cellulose recovery in less time relative to other processes and under reduced temperatures and pressures relative to dilute acid and ammonium explosion techniques, which reduces energy requirements/costs. Additionally, the solvent can be recycled at 94% efficiency and does not produce inhibitory products. However, some reports indicate that more cost effective recovery techniques are required.	<ul style="list-style-type: none"> <li>– University of Toledo</li> <li>– Joint BioEnergy Institute</li> </ul>
Carbon Dioxide Explosion	Supercritical carbon dioxide is used as an extraction solvent along with co-solvents such as ethanol-water or acetic acid-water to increase lignin removal. The process has the potential to reduce costs over ammonia explosion and since it is operated at lower temperatures, it does not cause degradation of sugars, such as those treated by steam explosion. However, another study concluded that despite its numerous advantages, it may be cost prohibitive for industrial applications.	<ul style="list-style-type: none"> <li>– Purdue University</li> <li>– Seoul National University, Korea</li> </ul>
IBUS Process – Continuous Hydrothermal Solution	At a high dry matter content, biomass is pretreated by steam and afterwards washed to remove potassium chloride, part of the hemicelluloses, and produced inhibitors with no additional chemicals which otherwise have to be recovered or neutralized. This reduces capital and operational costs as well as problems with corrosion.	<ul style="list-style-type: none"> <li>– Inbicon (Denmark)</li> </ul>
Wet Explosion	A combination of wet oxidation and steam explosion is used to pressure boil the biomass.	<ul style="list-style-type: none"> <li>– BioGasol</li> </ul>

\* Red = Identified by the Consortium for Applied Fundamentals Innovation (CAFI)

1/ Not an exhaustive list

## Step 2 – Hydrolysis

After the cellular structure has been opened up, enzymes or acids can then be used to break down the bonds and release fermentable sugars. The enzymatic hydrolysis of lignocellulosic biomass is far more challenging than that of the starch used in traditional corn-to-ethanol production. The hydrolysis of starch requires a single family of amylases, whereas, the hydrolysis of lignocellulosic material requires a number of different cellulases to deal with the interconnected matrix of cellulose, hemicellulose, and lignin. In this step, the hemicellulose is more easily hydrolyzed

than the cellulose, releasing mostly xylose sugars. However, the glucose sugars released from the cellulose are far easier to ferment (the next process step) than the xylose sugars.

Both acid hydrolysis and enzymatic hydrolysis methods are currently being developed. However, enzymatic hydrolysis is more suitable to homogeneous feedstock mixtures, whereas concentrated acid hydrolysis is more suitable for heterogeneous mixtures such as municipal solid wastes. Brief descriptions of a few of the hydrolysis processes currently being developed are provided below.

- *Dilute Acid Hydrolysis* - The dilute acid process is conducted under high temperatures and pressure and reaction time occurs in seconds to minutes, aiding in continuous processing. One drawback of this process is that despite process improvements, sugar degradation still occurs and yields are limited.
- *Concentrated Acid Hydrolysis*- Concentrated acid processes use lower temperatures and pressure, but reaction times are longer. There is little sugar degradation and the yield potential is higher than in the dilute acid hydrolysis process. However, in order to make this process more economical, sugar recovery and acid recycling must be optimized.
- *Enzyme Hydrolysis* - Enzymes, which are purchased or produced, are used to hydrolyze the pretreated biomass.
- *Direct Microbial Conversion (DMC)* - A hydrolysis process in which a single microorganism produces both ethanol and enzymes. DMC is further away from commercialization because researchers are still searching for a microorganism that produces sufficient ethanol and enzyme yields, but it has an advantage in that a dedicated process step for the production of cellulase enzymes is not needed, thus reducing overall process costs.

There have been significant advancements made over the past few years in regard to cellulase enzyme development, which has reduced the cost of these enzymes by a factor of 10-30, reducing overall costs down to 20-30 ¢/gal (figures cited from various sources within an EPA report<sup>20</sup>). However, it is estimated that these costs need to be reduced even further. Some analyses have suggested that these costs need to get down to 3-4 ¢/gal. However, developing these enzymes for a single, homogeneous feedstock may be easier than developing one for multiple feedstocks. This factor favors the development and use of abundant cellulosic biomass materials such as corn stover, at least in the short-term.

### **Combined Pretreatment and Hydrolysis**

Some of the more advanced pretreatments are done under conditions that would be amenable to enzyme stability and activity. This would enable the possibility of

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<sup>20</sup> EPA, 2009, "Draft of Regulatory Impact Analysis: Changes to Renewable Fuel Standard Program"

incorporating hydrolyzing enzymes into pretreatment stages, thereby combining the pretreatment and hydrolysis stages of cellulosic ethanol production. One of the more commonly reported approaches to cellulosic ethanol production using corn stover or corn fiber is that of using an acid pretreatment, whereby some of the hemicellulose is hydrolyzed, and then later, enzymes are used to hydrolyze the cellulose fraction.

### **Step 3 – Fermentation**

Once hydrolyzed, the glucose and xylose sugars can be co-fermented to ethanol. However, it is more difficult to effectively ferment the xylose sugars, and hence, there has been a great deal of effort directed toward the development of improved yeast strains/microorganisms that can efficiently co-ferment both xylose and glucose. While significant progress in this area has been achieved over the last few years, other issues such as microorganism sensitivity to inhibitors and the production of unwanted by-products continue to thwart the efficacy of these fermenting agents. Additionally, technology developers are also looking to lower the required dosage of the fermenting agent.

### **Combined Hydrolysis and Fermentation**

There are efforts underway by technology developers to combine hydrolysis and fermentation into a single step. Such efforts could significantly reduce capital costs by requiring fewer reactors and less supporting equipment and piping. The process could also reduce processing costs.

### **Step 4 – Product Separation and Distillation**

Once fermented, the ethanol is separated from the water and other by-products. Technology developments in this area are explored in more detail in Section III.G "Ethanol Distillation".

## **2. Market Potential**

The demand for cellulosic ethanol is in part supported by the Renewable Fuel Standard expanded by the Energy Independence and Security Act of 2007, which contained a 21 billion gallon mandate for advanced biofuels by 2022, including 16 billion gallons of cellulosic biofuel. Some cellulosic biofuel companies are focused on feedstocks other than corn, which offer greater environmental benefits and less impact on prices of major agricultural commodities; yet, corn biomass (e.g., corn stover, corn cobs, and corn fiber) will likely have a place in the mix of future feedstocks. Given the volume of ethanol that can be produced from corn starch and the interest in corn biomass as a cellulosic feedstock, this emerging technology has the potential to have a large demand impact on the corn sector.



### 3. Profiles - Companies & Research Institutions

There are numerous companies and research institutions developing their own approaches and unique technologies to cellulosic ethanol production via the biochemical platform, each with their own advantages and disadvantages. However, the bottom line is that a cost efficient process has yet to be commercialized. There are several companies that are expecting to reach commercialization by 2011/2012. Yet, the tight capital market is inhibiting many from obtaining the capital needed to go forth with their commercialization efforts.

Table 13 lists operational, under construction, and planned biochemical cellulosic ethanol facilities, as reported within a May 2009 EPA report<sup>21</sup>. Brief comments on a few of these companies and their technologies, along with a few other technology developers are included below.

#### **BioGasol**

BioGasol, along with its international partner Tate & Lyle, is working on a demonstration plant in Denmark, demonstrating the conversion of a wide array of feedstocks, including wood chips, garden waste, wheat and barley straw, energy crops and grass clippings. According to a March 2009 article in *Ethanol Producer Magazine*, BioGasol received \$13.4 million from the Danish Energy Agency's Energy Technology Development and Demonstration Program to fund the \$45 million project of building a 1.3 mmgy cellulosic ethanol demonstration facility in Aakirkeby, Denmark. Additionally, in the U.S., the company is collaborating with Pacific Ethanol and the Joint BioEnergy Institute to build a demonstration scale plant in Boardman, OR, for which it received \$24 million from the DOE in January of 2008. According to this March 2009 article, the company intends to have this U.S. plant completed by the fourth quarter of 2009.

BioGasol's cellulosic ethanol technology process is said to improve ethanol yields by 7.5%. The pretreatment process uses wet explosion, a combination of wet oxidation and steam explosion, essentially pressure boiling the biomass. Then, in the first bioreactor, enzymes from Novozymes hydrolyze the cellulose and hemicellulose into glucose and xylose, where the glucose is simultaneously fermented using industrial yeast. The xylose then goes to a second bioreactor, while the lignin is separated and pelleted as a fuel. In the second reactor, their novel thermophilic bacterium converts the xylose to ethanol and hydrogen. Any remaining organic material goes through a second anaerobic digester and is converted to methane. The company then uses its proprietary desalination technology so that the process water can be reused, minimizing water requirements.

#### **BlueFire**

While the EPA reported wood chips, grass cuttings, and yard waste as the feedstocks for the BlueFire cellulosic ethanol process, the company's website expands this list to include other feedstock forms as well, including agricultural

<sup>21</sup> EPA, 2009, "Draft of Regulatory Impact Analysis: Changes to Renewable Fuel Standard Program"



residues such as corn stalks and corn cobs, dedicated energy crops and paper. The company has been operating their pilot plant in California for roughly five years (not included in Table 13). According to the International Energy Agency, this pilot plant is at a 300 liter/day scale.

Their process uses a patented concentrated acid hydrolysis system and several other “improvements” that they claim make ethanol production more economical relative to older acid hydrolysis methods. According to the May 2009 EPA report, “Bluefire’s stated improvements include a more efficient acid recovery system; higher sugar purities and concentrations; use of more efficient microbes to ferment C6 (6 carbon) and C5 (5 carbon) sugars into ethanol; the processes ability to use biomass feedstocks containing silica.”

### **Mascoma**

In February 2009, Mascoma began production at its 20,000 gal/year demonstration plant in Rome, NY. The facility can utilize numerous feedstocks, including woodchips, grasses, corn stover and sugarcane bagasse.

Mascoma announced in May 2009 that they had made a major breakthrough in their consolidated bioprocessing (CBP) system. They have engineered microorganisms to produce cellulases and ethanol at a high yield in a single step. The Vice President of Mascoma’s Development and Operations division said that “these advances enable the reduction in operating and capital costs required for cost effective commercial production of ethanol, bringing Macoma substantially closer to commercialization.”

### **POET**

Poet, formerly Broin, has decided to use corn cobs as their primary cellulosic ethanol feedstock. Reasons for focusing on corn cobs over stover include: the collection will require minimal additional effort; it will not adversely affect soil quality, as the cob is only 15% of the above ground stover; it has higher carbohydrate content and it is a denser feedstock.

In January 2009, POET started-up operations at its 20,000 gal/year pilot scale plant in Scotland, S.D. The company now plans to expand production at its 50 mmgy grain-to-ethanol facility in Emetsburg, IA, to 125 mmgy, 25% of which is expected to be produced from corn fiber and corn cobs. This facility is expected to begin production in late 2011.

### **Vercipia (Verenium / BP)**

Verenium is focusing on grasses, energy cane, and bagasse as their key feedstocks. The company’s proprietary technology is capable of fermenting both 5-carbon (C5) and 6-carbon (C6) sugars. Verenium uses dilute acid steam explosion to hydrolyze the hemicellulose to C5 sugars. The C5 sugars are then washed and separated from the cellulose and are sent to the C5 fermentation process while the C6 sugars are sent to the C6 fermentation process. Then, the C5 and C6 beers are

blended together and run through a three stage distillation process to produce fuel grade ethanol.

Verenium and its joint venture partner, BP, have announced plans to build a 36 mmgy plant in Highlands County, FL. The companies intend to break ground in 2010 and begin production in 2012. They are calling the joint venture “Vercipia.”

### **ZeaChem**

ZeaChem uses a unique process that combines elements of biochemical and thermochemical cellulosic technologies. This hybrid process fractionates the biomass at the front-end, separating off the lignin. Glucose and xylose sugars are fermented into acetic acid (not ethanol), without releasing CO<sub>2</sub> as a by-product. Then, the acetic acid is converted to an ester and then reacted with hydrogen to get ethanol. This hydrogen stream comes from the gasification of the lignin separated out at the front-end, while the remaining syngas is burned to create steam and power for the system.

The company plans to begin construction of its 1.5 mmgy facility in Boardman, OR, this year, with an expected completion date in mid 2010.

### **Qteros**

Qteros, formerly known as SunEthanol, has announced “unprecedented” lab results from its proprietary conversion technology known as “C3” (Complete Cellulosic Conversion). The company plans to open up a pilot plant in Springfield, MA, this year. Lab results have shown that its Q Microbe can produce 70 grams of ethanol per liter of industrially pretreated biomass in a single step (combining hydrolysis and fermentation steps into one). The company states that “these unprecedented yield results far surpass the 50 grams per liter considered to be the threshold for commercial production of cellulosic ethanol.

Table 13: Biochemical Cellulosic Ethanol Plants (Operational, Under Construction, &amp; Planned)

Company / Plant Name	Location	Feedstocks	Prod Cap (MGY)	Est. Op. Date	Stage <sup>a</sup>	DOE Funding (for planned)
Abengoa Bioenergy Corporation	York, NE	Wheat straw, corn stover, energy crops	0.02	Sep-07	O	
Abengoa Bioenergy Corporation	Hugoton, KS	Corn stover, wheat straw, milo stubble, switchgrass	11.4	Early 2012	P	\$76 M
AE Biofuels	Butte, MT	Switchgrass, small-grain straw, corn stover	N/A	Aug-08	O	
Arkenol Technology Center	Orange, CA	Biomass	N/A	1994	O	
Auburn University / Masada Resources Group	Auburn, AL	Wood	N/A	1995	O	
BlueFire Ethanol, Inc.	Lancaster, CA	Woodchips, grass cuttings, yard waste	3.9	TBD	P	
BlueFire Mecca, LLC	El Sobrante, CA	Woodchips, grass cuttings, yard waste	17	TBD	P	\$40 M
BPI & Universal Entech	Phoenix, AZ	Paper waste (sorted MSW)	0.01	2004	O	
Cornell University's Biofuels Research Laboratory	Ithaca, NY	Perennial grasses, woody biomass	N/A	Jan-09	O	
DOE National Renewable Energy Laboratory	Golden, CO	Corn stover, other biomass	N/A	2001	O	
DuPont Danisco Cellulosic Ethanol	Vonore, TN	Corn cobs then switchgrass	0.25	Dec-09	C	
EcoFin / Alltech	Springfield, KY	Corn cobs	1.3	2010	P	\$30 M
ICM, Inc.	St. Joseph, MO	Corn fiber/stover, sorghum, switchgrass	1.5	2010	P	\$30 M
Macoma Corporation	Kinross, MI	Wood fiber	40	2012	P	\$26 M
Mascoma Corporation	Rome, NY	Wood chips	0.2	Feb-09	O	
Novozymes	Franklinton, NC	Corn stover	N/A	N/A	O	
Pacific Ethanol	Boardman, OR	Wheat straw, wood chips, corn stover	2.7	Early 2011	P	\$24 M
Pan Gen Global	Calusa County, CA	Rice straw and hulls	N/A	1995	O	
POET Project Bell	Scotland, SD	Corn cobs and fiber	0.02	Jan-09	O	
POET Project Liberty	Emmetsburg, IA	Corn cobs and fiber	25	End of 2011	P	\$80 M
POET Research Center	Scotland, SD	Corn cobs and fiber	N/A	N/A	O	
Pure Vision Technology, Inc	Fort Lupton, CO	Corn stover, wood, sugarcane bagasse	N/A	2003	O	
Pure Vision Technology, Inc	Fort Lupton, CO	Corn stover, wood, sugarcane bagasse	N/A	2009	O	
RSE Pulp and Chemical	Old Town, ME	Woody biomass	2.2	2010	P	\$30 M
Southeast Renewable Fuels LLC <sup>b</sup>	Clewiston, FL	Sweet sorghum, bagasse	20	End of 2010	P	
USDA Citrus & Subtropical Products Laboratory	Winter Haven, FL	Citrus residues	N/A	1990	O	
Verenium	Jennings, LA	Sugarcane bagasse	0.05	2006	O	
Verenium	Jennings, LA	Sugarcane bagasse, wood, energycane	1.5	Feb-09	O	
Verenium / BP	Lake Okeechobee, FL	Energycane, high-biomass sorghum	36	2011	P	\$ 10 M
Western Biomass Energy, LLC	Upton, WY	Wood waste (softwood)	1.5	2007	O	
ZeaChem	Boardman, OR	Wood chips, saw dust, logging debris	1.5	2010	P	

a/ O = Operational, C = Under Construction, P = Planned

b/ Biochemical or Thermochemical - process is unknown.

Source: EPA, 2009, "Draft of Regulatory Impact Analysis: Changes to Renewable Fuel Standard Program"

#### 4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to biochemical cellulosic ethanol technology development for the Minnesota corn industry.

**Table 14: SWOT – Cellulosic Ethanol – Biochemical Platform**

<b><u>Strengths</u></b>	<b><u>Weaknesses</u></b>
<ul style="list-style-type: none"> <li>▪ Very large market potential</li> <li>▪ Able to utilize C5 and C6 sugars.</li> <li>▪ Uses biomass - not limited to the corn kernel – averts food v. fuel debate.</li> <li>▪ Very strong institutional support</li> <li>▪ Relative to the thermochemical platform:               <ul style="list-style-type: none"> <li>○ Ability to carve out more value-added product streams – biorefinery concept.</li> <li>○ Less developed technology – more room from process improvements.</li> <li>○ Projected scale required is smaller. Larger scale requires feedstocks to be brought in from greater distances, which erodes economic competitiveness.</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>▪ Depending on the biomass (e.g., corn cobs, corn stover) utilized, some argue that soil erosion and soil quality issues can result.</li> <li>▪ Logistical cost issues associated with transporting the biomass.</li> <li>▪ Currently high production costs.</li> <li>▪ Not yet proven at a commercial scale. → Expected to approach commercial scale production in 2011/2012.</li> <li>▪ Does not allow for the production of a suite of traditional fuel products as does the thermochemical platform.</li> <li>▪ Very high capital costs relative to corn-based ethanol.</li> <li>▪ Benefits from this technology are not limited to corn; other sugar feedstocks can also be utilized – will depend on regional economics.</li> </ul>
<b><u>Opportunities</u></b>	<b><u>Threats</u></b>
<ul style="list-style-type: none"> <li>▪ High crude oil prices</li> <li>▪ Green funding – favorable policy environment</li> <li>▪ “Green product” marketability for chemical products produced from cellulosic ethanol biorefinery.</li> </ul>	<ul style="list-style-type: none"> <li>▪ Low crude oil prices</li> <li>▪ Economic competitiveness of alternative feedstocks</li> <li>▪ Tight capital markets</li> <li>▪ Over time, an EPA allowance for mid-level ethanol blending rates above the current 10%, or low costs for cellulosic ethanol production sufficient to allow high-level blends (e.g., E85), is necessary for cellulosic ethanol volumes to reach levels envisioned in the Renewable Fuel Standard.</li> </ul>

## D. Ethanol Distillation

### 1. Product/Technology Overview

The separation of alcohol and water is typically a costly, energy intensive process, representing a significant portion of the overall energy required by an ethanol facility. It is also one of the key cost components in the biochemical cellulosic ethanol platform. Traditionally, this separation is performed through a combination of steam distillation and a molecular sieve. However, there are various processes being developed whereby ethanol is removed during fermentation, reducing product inhibition and energy costs, and thereby also reducing greenhouse gas emissions. Alternative ethanol distillation technologies currently being developed include: vacuum stripping, gas stripping, membrane separation, solvent (liquid) extraction and supercritical CO<sub>2</sub>. These technologies are largely in the late development/early commercialization stage, and are expected to reach commercial status within 3-5 years, if not sooner.

**Vacuum Stripping** - The fermenting vessel is coupled with a vacuum chamber which extracts, in-situ, the more volatile ethanol and allows for partial product removal.

**Gas Stripping** - The fermenting broth overflowing from one stage to the next is contacted with a CO<sub>2</sub> stream that entraps the ethanol. The ethanol is then removed when this gas stream passes across a reactor and through an absorption tower where it is contacted with water. The CO<sub>2</sub> is then re-circulated. By using this process, the concentration of sugar in the product stream entering the fermenter is increased.

**Membrane Separation** - Membranes are used to filter the water/ethanol mixture during fermentation. The membranes are vapor phase separation units that allow the preferred permeation of water over other vapor components in a gas mixture.

**Solvent (Liquid) Extraction** - This approach removes the product that causes inhibition through an extractive biocompatible solvent that favors the migration of ethanol to solvent phase, a process known as extractive fermentation. However, it has been noted in one publication that this approach lowers solubility and results in a poisonous effect on yeast, thus restricting the development of this method.

**Supercritical Fluids** - While the success of separating alcohol and water via supercritical fluids has been demonstrated for many years, these previous demonstrations have not been able to compete with the economics of traditional steam distillation methods or other proposed methods such as membrane separation. However, MOR Supercritical has applied their supercritical extraction technology to ethanol dehydration, and claims a process that is scalable and cost-efficient relative to other proposed dehydration technologies.

## 2. Market Potential

Approximately 9.3 billion gallons of corn-based ethanol were produced in 2008, and given the current Renewable Fuel Standard, this production volume is expected to continue to grow along with that of cellulosic ethanol production. Yet, one of the areas in which technology can help improve the economic viability of this industry is in reduced energy consumption. In reducing the ethanol facility's energy consumption, not only are cost savings realized but greenhouse gas emissions are also reduced. And, while the outcome of a potential cap and trade system is uncertain, future economic incentives favoring lower carbon footprint facilities could further improve the economics of facilities implementing energy saving technologies.

Energy costs currently account for about 12% of overall operating costs, the second largest operating cost next to feedstock costs. Of the overall energy consumption, distillation and dehydration consume about 50% (McAloon et al., 2004; Kim and Dale, 2005 – cited by Vaperma). If an alternative ethanol technology reduced energy consumption of the distillation process by 40%, as several of the current technology developers claim to achieve, this would equate to an approximate 6¢ per gallon cost savings or \$3 million per year for a 50 mmgy ethanol facility (using current natural gas prices). If a royalty fee of 2 ¢/gal is assessed, as is the case with one technology developer, the cost savings for the 50 mmgy facility is still \$2 million per year. These are broad generalizations; the economics of advanced ethanol distillation will vary by individual technology.

## 3. Profiles - Companies & Research Institutions

While each of these methods has its own pros and cons, the leading technology at this time appears to be membrane separation, currently being pursued by Vaperma (Siftek) and Whitefox Technologies. Other technologies briefly reviewed below include Trans Ionics Corporation's extraction technology (ESep) and MOR Supercritical's supercritical CO<sub>2</sub> extraction technology. However, it is to be noted that there are also developments being made on gas and vacuum stripping technologies, as well as other solvent extraction methods.

### Vaperma

Vaperma is a Quebec based company that specializes in the development, manufacturing and commercialization of advanced gas separation systems. Their Siftek™ membrane separation technology can be integrated into new or existing ethanol plants to reduce energy costs and increase plant throughput. The Siftek™ membrane is a hydrophilic polymer membrane that can be used to dry ethanol in the vapor phase in a continuous process. The membrane system can replace both the rectification column and the molecular sieve unit in a conventional process. The feed gas flows into the membrane modules, which contain multiple hollow fibers packed



in a shell and tube configuration. The water vapor then permeates through the walls of the membrane and is vacuum pumped out (see Figure 20).

**Figure 20: Vaperma Siftek Distillation Technology Concept**



Source: Vaperma

Vaperma claims that their technology can increase overall fuel production by 15-20% and reduce energy consumption by up to 50% compared to traditional distillation and molecular sieves. By reducing the energy consumption, costs are reduced along with CO<sub>2</sub> emissions. For example, the company estimates that for a 40 mmgy ethanol facility, implementing the Siftek™ membrane system could reduce CO<sub>2</sub> production by 21,000 tons/yr. The company also claims that the technology has proven to be low maintenance, predicting that the membrane cartridge would not need replacing until after three years of continuous operation. Their technology was recognized by *Frost and Sullivan*, receiving the 2008 North America Technology Innovation of the Year Award.

The company has completed tests of its patented membrane separation technology, Siftek™, on a pilot scale (100K gal/yr) at a Greenfield Ethanol facility in Canada. Additionally, demonstration scale testing was just completed at a Greenfield Ethanol facility in Chatham, Ontario. According to a company representative, this demonstration was 8,000 liters per day (740K gal/yr).

Christian Roy, Vice President of Business Development for Vaperma, said that their membrane technology has immediate potential in ethanol market applications whereby the membrane is used as a replacement for molecular sieves for boosting or de-bottlenecking the current production process. Roy said that they had been in serious discussions to implement this technology in several commercial applications prior to the economic downturn, but that these companies have currently put this on hold given economic conditions. Several potential market applications for molecular sieve replacement by membrane technology are listed below.

- (1) Existing ethanol plants could use the membrane at the front end of current molecular sieve units (MSU) to boost the production capacity of a plant by roughly 16%, at half the expense of a new MSU. In this case, the payback period is estimated to be between 6 months and a year.
- (2) A new plant could use membranes in replacement of molecular sieves altogether. In this case, the payback period is less than 6 months.



- (3) Industrial ethanol production facilities could use membranes to help restore the 30% capacity that is lost when trying to increase the quality. Again, the payback period is estimated at less than 6 months.

As for replacing the rectification column, Roy estimated that it would be 2-4 years before the technology was commercially feasible, stating that while it is currently technically feasible it is not yet economically feasible. Roy explained that while it would be ideal to use membranes at the top of the beer column to separate the ethanol and water, you need a certain pressure differential to achieve efficient separation and beer columns are typically kept at low pressures to keep the temperature low (temperatures are kept low for a variety of reasons). And while there are ways to get around this problem, such as using a mechanical vapor compressor, these are expensive, and given current membrane costs, this route was said to be uneconomical at this point in time.

#### **Whitefox Technologies Limited**

Whitefox Technologies Limited, a London based company, has also developed an ethanol dehydration process using membrane separation. The company claims their continuous process is capable of dehydrating aqueous ethanol with a water content of 50-99.95% at atmospheric or elevated pressures without membrane saturation. The company says that they do not plan to commercialize their technology until it has been demonstrated in full-scale operations for four years. Currently, the company is testing their core technology in retrofitted and newly built plants, producing a combined total of 520 mmgy of ethanol.

#### **Trans Ionics Corporation**

Trans Ionics has developed a process they call ESep, which uses “proprietary extraction technology” to remove the ethanol from the water. The beer produced from the fermentation step, containing 3-15% alcohol, is fed to the ESep unit where an extraction process selectively removes the ethanol, producing a product stream that is typically 97+% ethanol. While a 60% reduction in energy consumption is estimated when incorporating the system into new ethanol and cellulosic ethanol plants, a 28% energy reduction and a 16 month payback period is estimated when retrofitting an existing ethanol plant. Additionally, the process is expected to reduce capital costs by eliminating the need for costly stainless steel distillation components. The company’s goals are to reduce capital costs and operating costs by 30% each versus their “next best competitor.” Trans Ionics’ business model for their ESep technology includes an estimated selling price of skid-mounted units for a 20 mmgy facility of \$1.25 million, plus a 2¢ per gal processing fee.

#### **MOR Supercritical CO<sub>2</sub>**

Another ethanol dewatering technology is MOR Supercritical's supercritical CO<sub>2</sub> process, which has the added benefit of CO<sub>2</sub> utilization. The company claims that their process is economically competitive with proposed membrane technologies. According to MOR's website, the company is currently seeking technology and

project development partners. They have already tested their technology in a small pilot unit are currently seeking a partner to install a large demonstration scale unit.

#### **4. SWOT**

The following is a summary of the strengths, weaknesses, opportunities and threats to ethanol distillation technology development for the Minnesota corn industry.

**Table 15: SWOT – Ethanol Distillation**

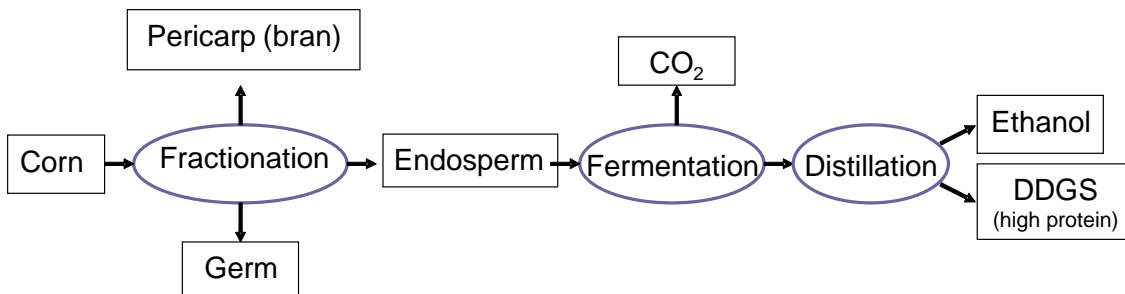
<p style="text-align: center;"><b><u>Strengths</u></b></p> <ul style="list-style-type: none"> <li>▪ Large market potential <ul style="list-style-type: none"> <li>○ Size of ethanol industry</li> <li>○ Strong potential impact on ethanol margins</li> </ul> </li> <li>▪ Moderate/strong institutional support</li> <li>▪ Moderate capital investment requirements</li> <li>▪ Increases plant throughput capacity</li> <li>▪ Reduces greenhouse gas emissions</li> <li>▪ Under the RFS as amended in 2007, this technology would help new or expanding ethanol facilities meet greenhouse gas reduction requirements.</li> <li>▪ Application as a molecular sieve replacement is deemed economical now – with a payback period of 6 months to a year for an existing ethanol facility.</li> </ul>	<p style="text-align: center;"><b><u>Weaknesses</u></b></p> <ul style="list-style-type: none"> <li>▪ Not yet proven at a commercial scale.</li> <li>▪ Cost advantage is heavily reliant on volatile natural gas prices.</li> <li>▪ Unknown economic viability as a complete distillation and dehydration system – company claims vary.</li> </ul>
<p style="text-align: center;"><b><u>Opportunities</u></b></p> <ul style="list-style-type: none"> <li>▪ High energy prices</li> <li>▪ Technology offers a potential advantage for existing ethanol producers – helps keep already existing infrastructure investments profitable.</li> <li>▪ Technology is at an early stage of commercialization with opportunities for process improvements.</li> <li>▪ A cap and trade system would further improve process economics relative to the traditional ethanol facility.</li> <li>▪ Could help ethanol utilization in California relative to other traditional Midwestern ethanol plants once the Low Carbon Fuel Standard goes into effect in 2011.</li> <li>▪ If the EPA grants an allowance for an ethanol blending rate of up to 15%, this will facilitate an increase in ethanol production.</li> </ul>	<p style="text-align: center;"><b><u>Threats</u></b></p> <ul style="list-style-type: none"> <li>▪ Low energy prices – reduces cost advantage</li> <li>▪ Tight capital markets</li> <li>▪ If the EPA does not grant an allowance for an ethanol blending rate of up to 15%, ethanol production volumes will be constrained by the current 10% “blend wall.”</li> </ul>

## E. Front-End Fractionation

### 1. Product/Technology Overview

Front-end fractionation separates the corn into three fractions including pericarp (bran/fiber), germ (the oil-bearing portion of the kernel) and endosperm prior to ethanol fermentation (see Figure 21). Currently, in dry mill ethanol production facilities, these other fractions go along with the starch into the fermentation vessel, taking up space and reducing production efficiency. A consequence of decreasing the unfermentable fraction of the corn during fractionation is to improve the fermentation efficiency and increase the ethanol yield (up to 12% according to some industry sources). Additionally, in the traditional ethanol process, the oil and the fiber end up in the distillers grains (DDGS) and are sold at feed ingredient prices of roughly 6.1¢/lb (March 2009). Whereas, their combined value if sold as separate co-products could be significantly greater. Another benefit of fractionation comes in the form of risk mitigation, as producers are not relying solely on the revenues from two product markets (i.e. ethanol and DDGS) and they have increased flexibility. Additionally, some technology developers claim, front-end fractionation can also reduce energy and water consumption, thus also reducing volatile organic compound emissions.

**Figure 21: Front-End Corn Fractionation**



Source: Informa Economics

As a result of removing the pericarp and germ from the front-end of the ethanol production process, the resulting DDGS are lower in fiber and oil and higher in protein. The high-protein DDGS obtained through fractionation can become a differentiated higher-value product. Yet, high-protein DDGS is a relatively new product and will require the development of a market. For that reason and since the lower oil content should in theory result in a lower energy value, it is expected that high-protein DDGS will trade at a price close to that of DDGS until such a market is developed and the value of the higher protein is proven.

Although the wet-mill industry benefits from large co-product value recovery, the dry-mill industry has tended to believe that these benefits could not be achieved without unacceptable increases in capital costs. However, over the years, there have been

numerous technological advancements that are moving front-end fractionation technologies for a dry-mill toward economical viability. Examples of companies currently using fractionation include:

- Lifeline Foods in St. Joseph, MO (50 mmgy)
- Poet in Coon Rapids, IA, (54 mmgy)
- Poet in Albert Lea, MN, (45 mmgy),
- Poet in Laddonia, MO, (50 mmgy), and
- Renew Energy in Jefferson, WI (130 mmgy).

There are several modified dry-mill fractionation processes, each with their own unique advantages and disadvantages. However, there are a few generalizations that can be made. These processes can generally be classified as either wet fractionation or dry fractionation processes.

In general, wet fractionation technologies tend to be more costly to implement. However, they also produce higher-valued co-products and there is less starch loss. The germ extracted by wet fractionation technologies has an oil content of approximately 40+% compared to 20-25% from typical dry fractionation technologies. This low oil germ produced by dry fractionation is sometimes referred to as “dirty germ,” and often wet mills and other oil extraction facilities are not geared to take germ with this low of an oil content. Yet, because corn oil extraction equipment is expensive and many companies do not want to handle hexane, most ethanol producers do not wish to extract the oil themselves. Additionally, the higher starch loss associated with the dry fractionation technologies is a revenue factor for the ethanol producer, as ethanol yields are compromised. Nonetheless, dry fractionation technologies are more prevalent in current plant installations, primarily due to cost differences.

The company MOR Technology claims to have developed a fractionation process, MOR FRAC+, with the costs generally associated with dry fractionation technologies but the higher valued co-products and the lower starch loss generally associated with wet fractionation technologies. While unproven at a commercial scale, this process appears to have promise.

## 2. Market Potential

Front-end fractionation offers the ethanol producer several ways in which to increase ethanol margins and reduce risk. Estimates of net income increases range from 9-28 ¢/gallon, while estimates of capital costs range from 17-70 ¢/gallon of capacity. These estimates range across the various technologies and depend on input cost and co-product value assumptions<sup>22</sup>. Given these company-provided estimates, the payback period for front-end fractionation is generally less than 2 years.

<sup>22</sup> Most of the underlying value assumptions for the high protein DDGS behind the income estimates are significantly higher than traditional DDGS. However, as discussed previously, high-protein DDGS is a relatively new product and will require market development, and for that reason, it is expected

While there are also back-end fiber and oil extraction technologies that are either currently available or being developed that are less expensive, these processes do not produce the high revenue co-products that are generated from front-end fractionation. For example, the oil that is extracted at the back end of the process typically cannot be used in food products and is thereby a lower valued product. Additionally, there are ethanol production efficiencies that are gained when the starch fraction is separated out at the beginning of the process.

The following section profiles a few of the front-end fractionation technologies currently available, detailing where information is available, production parameters, net income impacts, and capital cost requirements.

### **3. Profiles - Companies & Research Institutions**

As much quantifiable data as could be uncovered via desk research and personal interviews at the time of this report are provided in the profiles below. Many of the following companies/institutions make claims on their websites or within press releases that are similar in nature; examples include:

- lower capital cost requirements
- reduced operational costs
- increased protein and reduced fiber and oil content of DDGS
- reduced energy and/or water consumption
- reduced fermentation time
- increased capacity
- increased co-product value

However, this information was only included in the profiles below if quantifiable claims were made.

#### **Modified Dry-Mill Wet Fractionation Technologies**

Wet fractionation technologies typically involve soaking/steeping the corn prior to fractionation. In general, the capital costs are higher than that of dry fractionation technologies, but the starch loss is lower and the quality/value of co-products is higher.

- ♦ **Corn Value Products (CVP) / Quality Technology International Inc.** – Quality Technology is heading the marketing efforts of CVP's wet fractionation system, HydroMilling. The system produces a suite of co-products marketed under the brands "Prairie Sky" and "Solaris".

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that high-protein DDGS will trade at a price close to that of DDGS until such a market is developed and the value of the higher protein is proven.

- ♦ **Maize Processing Innovators (MPI) / FCStone Carbon** – The Quick Germ (QG) wet fractionation technology was originally developed by the University of Illinois. This process was later enhanced to fractionate both the germ and the pericarp fiber, and is known as the Quick Germ Quick Fiber (QGQF) process. The license for the technology is now held by MPI which has an agreement with FCStone Carbon LLC to lead commercialization efforts. According to an online presentation on MPI's website, quantifiable claims include:
  - The process yields approximately 3.1-3.7 lbs/bu of germ; 3.3-4.0 lbs /bu of fiber; and 10.3-11.6 lbs/bu of low fat, low fiber DDGS
  - Minimum oil content of germ is 38%
  - Maximum 3% starch loss
  - Crude protein content of DDGS = 49.31%, fat content ~3.85%; ash = 3.24%; and ADF = 6.80%; compared to 28.5%, 12.7%, 5.32% and 10.80%, respectively, with traditional dry grind technology (no fractionation)
- ♦ **University of Illinois** – The University of Illinois has since made process improvements to the QGQF process, developing what they call enzymatic milling, also known as E-Mill. In addition to recovering the germ and the pericarp fiber, the E-Mill process also recovers the endosperm fiber; this further reduces the quantity of DDGS produced to 65-70% of the conventional dry-grind process. However, the E-Mill process also adds an additional enzyme to the process. Whereas the QGQF only requires amylase, the E-Mill process requires both amylase and protease.
  - According to data from University of Illinois professor Vijay Singh: crude protein content of DDGS = 58.5%, fat content =4.5%; ash = 3.2%; and ADF = 2%
  - In an Agriculture Research Service (ARS) study comparing the E-Mill process to conventional dry grind, the E-Mill process:
    - increased fermentation capacity by 27%,
    - reduced fiber content of DDGS by 81%, and
    - increased the protein content of DDGS by 105%.

### **Modified Dry-Mill Dry Fractionation Technologies**

Dry fractionation technologies typically separate the germ and fiber from the corn kernel mechanically without the need for soaking. In general, capital costs are lower than that of wet fractionation technologies, but starch loss is higher and the quality/value of co-products is lower.

- ♦ **Renessen LLC.** – Renessen is a joint venture between Cargill and Monsanto. Renessen is currently operating a pilot facility using their Extrax Processing System at Cargill's BioProcessing Center in Eddyville, IA, processing 10,000 bushels of corn per day. Meanwhile, Monsanto is in the fourth and final stage prior to product launch of their high oil corn (7% compared to 3.5%) for use in Renessen's Extrax corn fractionation system. They are focusing on higher oil content as this is the most valuable fraction of the corn. According to a 1<sup>st</sup> quarter



2009 issue of *Distillers Grains Quarterly*, company vice president Michael Morgan expects their first commercial facility to be in place within two years.

- ♦ **Cereal Process Technologies** – Cereal Process Technologies has installed its patented dry fractionation technology in several dry-grind corn mills, including Renew Energy LLC's 130 mmgy facility in Jefferson, WI. Quantifiable company claims include:
  - 35% reduction in drying costs – reducing energy consumption to 21,000-22,000 BTU/gal.
  - Water consumption is reduced to 2.7 gallons per gallon of ethanol (33% savings).
  - Each module processes 650-800 bu. of corn per hour, but 650 is the “sweet spot”.
  - The use of their new “MarketFlex” enables producers to adjust the amount of oil versus starch they want in order to better respond to market price fluctuations.
  - Resulting DDGS contain about 40% crude protein.
  - Capital costs will vary, but are estimated at \$30 million for a nine-module system such as the one installed at Renew Energy. The estimated payback for this system was two years.
  - The technology can add more than 20 ¢/gal to the producer's net income.
  - Yield: germ = 12.5%; bran = 7.5%; and endosperm = 80%
- ♦ **Delta-T Corp. / Ocrim Milling** – Delta-T and Ocrim Milling have developed a dry fractionation technology known as “Dry Separation Technology.” The process works by using a degerminator to separate the germ from the corn kernel by forcing the kernel against a stationary screen, which contains holes large enough to push the germ fraction through but small enough to prevent the endosperm from passing through. Then, the fiber and the endosperm are fractionated by using a series of roller mills and vibrating screens. Quantifiable company claims include:
  - Guaranteed maximum starch loss of 4%
  - Guaranteed minimum increase in throughput capacity of 10% for an existing Delta-T designed facility
  - 6,000 BTU/gal reduction in energy use
  - Neal Jakel, Fractionation Program Manager for Delta-T Corp, believes fractionation can reduce operational costs by 8-15 ¢/gal.
- ♦ **Crown Iron Works Co.** – This Minnesota based company has developed a dry fractionation and corn oil extraction system (Crown solvent extraction and oil refining system). The fractionation system is a combination of de-germinators, aspirators, screeners and roller mills in sequence to refine a germ and starch stream from whole corn. ICM has recently agreed to have Crown Iron Works as their preferred technology provider.

- ♦ **Poet-BFRAC / Satake Corp.** – There are several ethanol facilities currently using Poet’s Bfrac system. The resulting DDGS created from this system are marketed as Dakota Gold HP.
- ♦ **FWS Technologies** – FWS Technologies is a Canadian based company that has developed and patented a dry fractionation system they call “FWS Fractionation System”.
  - Yields: germ = 4.4 lbs/bu (8%); bran = 3.4 lbs/bu (6%); endosperm = 48.2 lbs/bu (86%); DDGS = 12.5-13 lbs/bu
  - Crude protein content of DDGS = 35-37%, fat content = 6.5%; ash = 3.8%; and NDF = 21%
  - Starch loss = 5%; ethanol yield 2.66 gal/bu
  - Capacity increase = 12%
  - Capital cost ~ \$10 million for a 57 mmgy ethanol facility
  - Increased net income is estimated to be ~25¢/gal

### **MOR Technology’s MOR Frac+**

MOR Frac+ is promoted as a "second generation fractionation" process with the product separation and co-product quality advantages of wet fractionation technologies and the lower capital and operating costs typical of dry fractionation technologies. The process utilizes parts of MOR’s original dry separation technology at the front of the process and then uses various wet milling steps to further refine and separate the products. In this way the original MOR technology is combined with Corn Value Products’ wet separation technology, HydroMilling.

The company claims that rather than having to sell the “dirty germ” into the animal feed market and receive lower than typical DDGS prices, as is the concern with dry fractionation systems, their system produces a high quality germ that exceeds wet milling germ specifications (germ oil yield is 40-45%), which can be sold as food-grade. Additionally, the company claims that compared to the dry fractionation systems, their technology results in lower starch loss (less than 2%), near zero sugar loss, does not require additional water use, and requires fewer additional nutrients. The DDGS produced also has a higher protein content (58+ %) than that produced from dry fractionation and even some wet fractionation systems. In comparison to wet fractionation systems, the company claims that their process produces a higher quality germ, uses less energy and water and requires less capital.

The MOR system is 20-40% more expensive than the average fractionation system, at a cost of about \$35 million for a 50 mmgy ethanol facility, but MOR claims that the payback period is shorter.

“In a recent analysis of a typical 55 mmgy plant operating over the past year, MOR’s fractionation design could have generated an additional \$14 million in net income over this span or an average of \$0.28 per nameplate

gallon<sup>23</sup>. Put another way, when ethanol sells for \$1.60/gal, a producer's breakeven price for corn may be close to \$3.70/bu. With MOR's system, however, the breakeven price is increased to \$5.00/bu." (*Trade and Industry Development*)

MOR also offers an additional technology package whereby the CO<sub>2</sub> produced from the ethanol facility is captured and converted to supercritical CO<sub>2</sub>, a solvent which is then used to remove the corn oil from the germ. As opposed to conventional supercritical processes, MOR Supercritical claims that their technology greatly reduces operating costs which have prevented other supercritical systems from replacing petrochemical extraction using hexane. MOR Supercritical claims that their technology is energy efficient; automated, modular and scalable; has a small environmental footprint (1/6 of a typical solvent extraction plant); produces safe, solvent-free, non-degraded, high-quality products including un-degraded meal with high protein digestibility; and has an accompanying refining technology to extract and refine the oil in one step.

MOR states that the \$0.28/gal increase in profit generated from using MOR's fractionation system could be increased by an additional \$0.10/gal as food markets are maximized and the CO<sub>2</sub> oil extraction process is added.

According to an April 2009 article in *Ethanol Producer Magazine*, "MOR Technology doesn't have its patent-pending system installed in any ethanol plants yet, but the company has a pilot fractionation plant in the SEMO Mill in Scott City, MO.

#### 4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to front-end fractionation technology development for the Minnesota corn industry.

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<sup>23</sup> MOR claims that this 28 cent/gallon estimate is based off of fairly conservative values for co-products, "recognizing that some are newer and it may take time to establish values (*Ethanol Producer Magazine*, April 2009).

**Table 16: SWOT – Front-End Fractionation**

<p style="text-align: center;"><b><u>Strengths</u></b></p> <ul style="list-style-type: none"> <li>▪ Large market potential <ul style="list-style-type: none"> <li>○ Size of ethanol industry</li> <li>○ Potential impact on ethanol margins</li> </ul> </li> <li>▪ Strong institutional support</li> <li>▪ Certain individual technologies have already been proven at commercial scale.</li> <li>▪ Increases plant throughput/capacity</li> <li>▪ Reduces greenhouse gas emissions</li> <li>▪ Under the RFS as amended in 2007, this technology would help new or expanding ethanol facilities meet greenhouse gas reduction requirements.</li> <li>▪ Risk mitigation <ul style="list-style-type: none"> <li>○ More than two revenue sources</li> <li>○ Increased flexibility</li> </ul> </li> <li>▪ Corn oil is favored relative to other oils in certain foods as it does not require partial hydrogenation which results in trans fats.</li> </ul>	<p style="text-align: center;"><b><u>Weaknesses</u></b></p> <ul style="list-style-type: none"> <li>▪ Depending on the individual technology, capital costs could be 17-70 ¢/gal.</li> <li>▪ Reduced yield due to starch loss – more so with dry than wet fractionation technologies</li> <li>▪ With dry fractionation – “dirty germ” may become a problem – extraction facilities don’t want it and on-site extraction costs can be uneconomical.</li> <li>▪ Need to find an oil extraction facility to extract the oil.</li> <li>▪ If oil is extracted on site - oil marketing issues may arise.</li> <li>▪ Greater marketing capabilities are required to handle multiple product streams – weakness for facilities lacking such skills or opportunities.</li> </ul>
<p style="text-align: center;"><b><u>Opportunities</u></b></p> <ul style="list-style-type: none"> <li>▪ High vegetable oil prices</li> <li>▪ There is still room for process improvements</li> <li>▪ There are several developments being made regarding new uses for fiber.</li> <li>▪ A cap and trade system would further improve process economics.</li> <li>▪ If EPA grants an allowance for an ethanol blending up to 15%, ethanol production has room to increase.</li> <li>▪ Growing vegetable oil demand stemming from population growth and biodiesel industry.</li> <li>▪ Benefit for facilities with the greater marketing capabilities required to handle multiple product streams.</li> <li>▪ Technology offers a potential advantage for existing ethanol producers – helps keep existing infrastructure investments profitable.</li> </ul>	<p style="text-align: center;"><b><u>Threats</u></b></p> <ul style="list-style-type: none"> <li>▪ Low vegetable oil prices</li> <li>▪ Tight capital markets</li> <li>▪ If the EPA does not grant an allowance for an ethanol blending rate of up to 15%, ethanol production volumes will be constrained by the current 10% “blend wall.”</li> <li>▪ If all ethanol facilities incorporated the technology, co-product values will be depressed.</li> <li>▪ High protein, low fiber, low fat DDGS may not be valued at a premium to traditional DDGS, particularly in monogastrics.</li> </ul>

## F. 3-Hydroxypropionic Acid (3-HPA)

### 1. Product/Technology Overview

3-Hydroxypropionic acid (3-HPA) is a building block chemical that can be used to produce many other commodity and specialty chemicals used in a wide array of product applications, including solvents, plastics and moldings, fibers and resins, composites, adhesives, coatings, aliphatic polyesters and copolyesters and disinfectants. One of the most promising aspects of this building block chemical is not only the current petrochemical markets which it could potentially replace, but also the new and unique chemical properties it would bring to the market. Given its potential, it was identified by the U.S. DOE in 2004 as one of the top 12 chemicals from biomass sugars and syngas.

Unlike some of the other building block chemicals, there are no petrochemical production routes to 3-HPA. However, many of the derivative chemicals that can be produced from 3-HPA are now commercially produced from fossil fuel feedstocks. 3-HPA can be converted into a variety of high-value chemicals, including acrylic acid, 1,3-propanediol, malonic acid, acrylamide, methyl acrylate, acrylonitrile, propiolactone, and ethyl 3-HPA. Table 17 provides an overview of potential derivatives and applications of 3-HPA, as well as the companies/institutions involved in its development.

**Table 17: 3-HPA – Derivatives, Applications, and Institutions/Companies Involved**

Derivatives <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/Companies Involved <sup>1</sup>
<ul style="list-style-type: none"> <li>- 1,3-Propanediol</li> <li>- Acrylic Acid</li> <li>- Methyl Acrylate</li> <li>- Acrylamide</li> <li>- Malonic Acid</li> <li>- Ethyl 3-HP</li> <li>- Propiolactone</li> <li>- Acrylonitrile</li> </ul>	<ul style="list-style-type: none"> <li>- Solvents</li> <li>- Plastics and moldings</li> <li>- Fibers and resins</li> <li>- Composites</li> <li>- Adhesives</li> <li>- Laminates, floor polishes, paints and coatings</li> <li>- Aliphatic polyesters and copolyesters</li> <li>- Wastewater treatment, gel electrophoresis, papermaking, ore processing, and the manufacture of permanent press fabrics.</li> <li>- Vitamins</li> <li>- Disinfectant; has been used to sterilize blood plasma, vaccines, tissue grafts, surgical instruments, and enzymes.</li> </ul>	<ul style="list-style-type: none"> <li>- Cargill<sup>2</sup></li> <li>- Codexis</li> <li>- Pacific Northwest National Laboratory</li> <li>- Novozymes</li> <li>- U.S. Department of Energy</li> <li>- Qingdao Institute of Biomass Energy and Bioprocess Technology (China)</li> <li>- Perstorp</li> </ul>

Source: Informa Economics

1/ Not an exhaustive list

2/ Recently, Cargill has said that they have decided not to further pursue the development of 3-HPA

## 2. Market Potential

The market potential for 3-HPA lies in the numerous applications for which its derivatives can be used. Acrylic acid is the derivative that is currently receiving the most attention, as it is a high value, high volume chemical used in a wide array of products, such as plastics, fibers, coatings, adhesives, paints, and superabsorbent polymers<sup>24</sup>. Currently, acrylic acid is primarily produced by oxidation of propylene, a petrochemical feedstock. The acrylic acid market is approximately 3 million metric tons<sup>25</sup>, with almost half of this going toward the production of glacial acrylic acid for superabsorbents, which is largely used to produce personal care items such as diapers (more than 1 million tons annually)<sup>26</sup>. Additionally, the acrylic acid market grows approximately 4% per year<sup>26</sup>. According to ICIS Pricing, the August 2008 acrylic acid price was \$1.10-1.15/lb.

According to an August 2008 ICIS market report, the acrylic acid market is growing at an average annual rate of 3.4% (2002-2007). The report also stated that 55% of the acrylic acid is used to produce acrylate esters, which are used primarily in architectural and industrial coatings, but also in adhesives, paper and leather coatings, polishes, carpet backing compounds, and tablet coatings. Forty-two percent of the acrylic acid produced is used to make polyacrylic acid and salts, with approximately 83% of this being used to make superabsorbents (ICIS). However, according to their market report, this market is now saturated. Yet, they identified “soaker pads” used in food packaging for poultry, meat, fish, fruits and vegetables as a new market application.

Acrylamide is another derivative that can be produced from 3-HPA. Acrylamide, which is classified as a resin, is used to synthesize polyacrylamides which are used as water-soluble thickeners. Applications include: wastewater treatment, gel electrophoresis, papermaking, ore processing, and the manufacture of permanent press fabrics. According to a 2003 report by the DOE, cited on the Wisconsin Biorefining Development Initiative’s website, the market for acrylamide derivatives (e.g., polyacrylamide, styrenebutadiene latex, acrylic resins, and other comonomers) is 206 million pounds per year, at a market price of \$1.76-1.86/lb.

## 3. Profiles - Companies & Research Institutions

### **Cargill, Codexis, Pacific Northwest National Laboratory and Novozymes**

Cargill, along with Codexis and the Pacific Northwest National Laboratory (PNNL), have developed a bioprocess to produce 3-HPA which converts glucose or other carbohydrate sources into 3-HPA using a multi-step enzymatic reaction within the

<sup>24</sup> Superabsorbent polymers were mentioned as a large potential market for starch derived products during an interview with USDA, Agricultural Research Service.

<sup>25</sup> 2005 acrylic acid market estimates ranged from 2.99 million MT (DOE) to 3.1 million MT (Cargill).

<sup>26</sup> Source: Cargill. January 14, 2008 press release



cells of a microorganism. Cargill already has patents related to its biobased 3-HPA production process.

In early 2008, Cargill announced a joint agreement with Novozymes to develop technology enabling the production of acrylic acid via 3-HPA, supported by a \$1.5 million matching cooperative agreement from the DOE. At the time of the announcement, the companies said they expected their technology to produce 3-HPA and its derivatives, such as acrylic acid, to be ready in 5 years (2013).

According to a 2005 DOE presentation, acrylic acid production via this biochemical route could result in an advantage of more than 5 ¢/lb over propylene oxidation for a Midwest plant (West Texas Intermediate crude oil 2005 average = \$56.5/bbl).

However, according to an interview with Bill Brady, director of media relations for Cargill, the company has recently decided not to further pursue the development of 3-HPA. According to Brady, this decision was not a result of recent economic conditions, nor a reflection on 3-HPA's market potential, but rather, they did not feel that given their core area of expertise that they would be able to bring the technology to commercialization within a reasonable time frame. Such a response may indicate that this product/technology may be more of long term prospect.

#### **Perstorp**

According to *Chemical and Engineering News*, Perstorp, a Swedish based specialty chemical firm, has a five year project to study the manufacture of natural raw-materials based 3-HPA.



## 4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to 3-HPA technology development for the Minnesota corn industry.

**Table 18: SWOT – 3-Hydroxypropionic Acid**

<b><u>Strengths</u></b>	<b><u>Weaknesses</u></b>
<ul style="list-style-type: none"> <li>▪ Large market potential</li> <li>▪ Technology to develop 3-HPA already exists.</li> <li>▪ Green process that provides an alternative to petrochemicals</li> </ul>	<ul style="list-style-type: none"> <li>▪ The largest source of institutional support behind 3-HPA has recently decided not to further pursue its development. There is no word yet if their partners, Novozymes or PNNL, will continue.</li> <li>▪ Technology to develop derivatives from 3-HPA is still being developed.</li> <li>▪ Not yet proven at a commercial scale.</li> <li>▪ Benefits from this technology are not limited to corn; other sugar feedstocks can also be utilized – will depend on regional economics.</li> </ul>
<b><u>Opportunities</u></b>	<b><u>Threats</u></b>
<ul style="list-style-type: none"> <li>▪ High crude oil prices</li> <li>▪ Might be an opportunity for a company/institution to further build upon the intellectual foundation already established by Cargill.</li> <li>▪ In addition to acrylic acid, other high value, high volume chemical derivatives could also be developed.</li> <li>▪ First mover advantage allows early market entrants the opportunity to capture premium prices in higher value-added markets.</li> <li>▪ “Green product” marketability for chemical product applications (e.g., solvents) – may command small premium in niche markets/products.</li> <li>▪ Biobased products could help meet LEED certification requirements.</li> <li>▪ Growing world demand for plastics and other biobased products.</li> <li>▪ Biobased products may qualify for the USDA BioPreferred program.</li> </ul>	<ul style="list-style-type: none"> <li>▪ Low crude oil prices</li> <li>▪ High feedstock costs</li> <li>▪ Biobased 1,3-propanediol is already produced at a commercial scale. It is unclear as to whether its production via 3-HPA could be economically viable in the future.</li> <li>▪ Tight capital markets</li> <li>▪ Cargill may be unwilling to share intellectual property – outside company/institution would have to “reinvent the wheel.”</li> <li>▪ Favorable economic competitiveness of non-corn based 3-HPA.</li> </ul>

## G. Succinic Acid

### 1. Product/Technology Overview

Succinic acid is a building block chemical that can be used to produce many other commodity and specialty chemicals used in a wide array of product applications, including solvents, coatings, adhesives, plastics, fibers, lubricating oils, diesel fuel oxygenates, personal care products and cosmetics (see Table 19). While succinic acid is currently commercially produced via petrochemical production routes in small quantities, biobased production routes are currently being developed by numerous companies and research institutions. If a technology is developed and proven at commercial scale to produce biobased succinic acid that is cost competitive with similarly functioning petrochemicals, the potential world market for this four carbon dicarboxylic acid is in excess of \$1 billion per year.

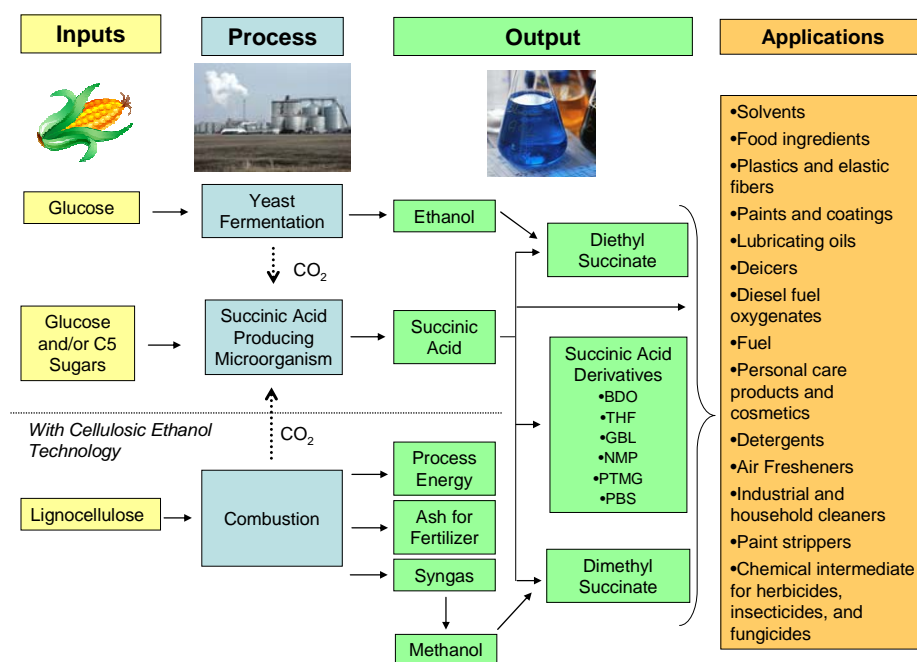
In addition to the many market applications for which succinic acid and its derivative chemicals can be applied, another promising attribute is that its production requires CO<sub>2</sub>, leading to what some claim to be as a carbon negative process. While there are various renditions of possible succinic acid biorefinery concepts, Figure 22 illustrates one such concept. Biobased succinic acid is produced by converting the glucose and/or five carbon sugars from a variety of possible feedstocks, including corn, using a specific succinic acid fermenting microorganism and CO<sub>2</sub>. Once succinic acid is produced, a variety of other chemicals can then be derived, each with their own list of potential market applications.

**Table 19: Succinic Acid – Derivatives, Applications, and Institutions/Companies Involved**

Derivatives <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/Companies Involved <sup>1</sup>
<ul style="list-style-type: none"> <li>– 1,4-Butanediol (BDO)</li> <li>– Tetrahydrofuran (THF)</li> <li>– γ-Butyrolactone (GBL)</li> <li>– 2-Pyrrolidinone</li> <li>– N-Methyl Pyrrolidone (NMP)</li> <li>– Polytetra-methylene Glycol (PTMG)</li> <li>– Poly-Butylene Succinate (PBS)</li> <li>– Diethyl and Dimethyl Succinate (Succinic Acid + Ethanol/Methanol)</li> </ul>	<ul style="list-style-type: none"> <li>– Solvents</li> <li>– Food ingredients, flavors</li> <li>– Plastics and elastic fibers, including Nylon-4,6; films, sheets, filaments, laminates, molded foam products, and injection-molded products</li> <li>– Paints and coatings, including as a resin solvent in wood stains and varnishes</li> <li>– Lubricating oils, engine coolants and deicers</li> <li>– Diesel fuel oxygenates</li> <li>– Personal care products and cosmetics</li> <li>– Detergents, air fresheners and household cleaners</li> <li>– Automotive and industrial cleaners</li> <li>– Paint strippers and graffiti removers</li> <li>– Chemical intermediate for herbicides, insecticides and fungicides</li> </ul>	<ul style="list-style-type: none"> <li>– Agro Industrie Recherches et Développements (ARD), France</li> <li>– DNP Green Technology</li> <li>– Bioamber (JV: DNP and ARD)</li> <li>– US Department of Energy</li> <li>– National Research Council of Canada Biotechnology Research Institute</li> <li>– Rice University</li> <li>– Roquette and DSM</li> <li>– University of Georgia</li> <li>– Toyota Tsusho Company, Japan (shareholder of Bioamber)</li> <li>– Michigan State University, Michigan Biotechnology Institute</li> <li>– BioEnergy International (Myriant Technologies)</li> <li>– Mitsubishi Chemical Corporation</li> </ul>

Source: Informa Economics

1/ Not an exhaustive list

**Figure 22: Succinic Acid Biorefinery Concept**

Source: Informa Economics

## 2. Market Potential

The potential of succinic acid has been recognized by many countries and was identified by the DOE in 2004 as one of the top 12 chemicals from biomass sugars. Furthermore, this chemical can be used to produce other top 12 chemicals.

Succinic acid is currently commercially produced via petrochemical feedstocks (e.g., n-butane via maleic anhydride). Worldwide market estimates for the current succinic acid market vary widely, from 15,000 MT/yr to 50,000 MT/year. Yet, while estimates of the current market size vary from one source to another, industry representatives consistently agree that the potential for this market is much larger.

- In a 2007 article in *Biomass Magazine*, Susanne Kleff, a senior scientist for MBI International, stated that the market potential for biobased succinic acid was well over 100 times its current market of 15,000 MT/year.
- A 2008 USDA report, "U.S. Biobased Products Market Potential and Projections Through 2025," which Informa and MBI International were involved in writing, stated that the succinic acid market could "easily exceed \$1 billion per year by 2015."
- Dilum Dunuwila, vice president for business development at Bioamber, a biobased succinic acid technology developer, believes that succinic acid could potentially become a \$50-70 billion market in 10-20 years.
- According to the website of BioEnergy International, another biobased succinic acid technology developer (which has recently formed Myriant Technologies to develop biobased products), the total immediate addressable market for succinic acid is in excess of \$7.2 billion.

Current petrochemical production processes for succinic acid and its derivatives are not cost competitive with other petrochemicals, and thus, succinic acid is currently a high cost chemical that serves only in niche market applications. However, if a cost competitive biobased production route for succinic acid were developed, succinic acid could potentially serve as a replacement or partial replacement for many petrochemicals currently on the market. One such chemical in which succinic acid could potentially serve as a partial replacement is maleic anhydride, a chemical with a current global market of about 1.65 million tons (Kleff, 2007). However, succinic acid is not suitable for all maleic anhydride applications. Succinic acid could also serve as a potential replacement for other petrochemicals, including 1,4-butanediol (BDO), a chemical with a 1.2 -1.4 million MT/yr market, as well as adipic acid, a 2.4-2.8 million MT/yr market (Dunuwila, personal communication). Other derivative markets include tetrahydrofuran (THF),  $\gamma$ -butyrolactone (GBL), 2-pyrrolidinone, N-methyl pyrrolidone (NMP), polytetramethylene glycol (PTMG), poly-butylene succinate (PBS), and diethyl and dimethyl succinate (succinic acid + ethanol/methanol). Potential market applications for these chemicals include, but are not limited to, solvents, coatings, adhesives, plastics, fibers, lubricating oils, diesel fuel oxygenates, personal care products and cosmetics (see Table 19).

### 3. Profiles - Companies & Research Institutions

There are several companies and research institutions currently developing biobased production routes to produce succinic acid and its derivatives from a variety of renewable feedstocks containing sugar (see Table 19). The majority of the research focus has been concentrated on developing higher yielding microorganisms. Yet, there has also been significant effort directed toward reducing downstream processing costs. Many of the succinic acid producing microorganisms produce at least some quantity of by-products (e.g., acetic acid, formic acid, lactic acid and pyruvic acid) that must be removed/separated from the succinic acid. In a 2008 literature review of succinic acid, Bechthold et al. stated that the “downstream purification cost for fermentation-based processes normally amounts to more than 60% of the total production costs.”

#### **DNP Green Technology and ARD - Bioamber**

DNP Green Technology has partnered with Agro Industrie Recherches et Développments (ARD) to form Bioamber, with Toyota Tsusho Corporation as a strategic shareholder. The company also has ongoing relationships with the DOE, Oak Ridge National Laboratories, Michigan State University, and Biotechnology Research Institute of Montreal. Bioamber is using a strain of *E. coli* developed by the DOE in the mid 1990s and has developed a technology for the separation and purification of succinic acid. The current strain of *E. coli* can be used to produce succinic acid from glucose and 5-carbon sugars. Additionally, if cellulosic ethanol technologies are developed to where 6-carbon sugars from wood chips can be economically produced, the *E. coli* strain will be able to use this sugar form as well. However, sucrose must first be hydrolyzed before it can be utilized.

Bioamber claims to be the “first company to successfully develop a commercially viable technology for the production of succinic acid by fermentation of various renewable feedstocks,” claiming to be 2-3 years ahead of their competition. According to Dunuwila, Bioamber’s succinic acid technology is cost competitive with petrochemically produced succinic acid, and is close to being competitive with petrochemical alternatives at \$65/barrel crude oil, at the demonstration scale. The company currently has a pilot facility in France and construction of its 2,000 MT/yr, \$27 million demonstration facility is already underway. The facility will be integrated with a wheat refinery for glucose, utilities, and waste handling and can utilize CO<sub>2</sub> from the 90 mmgy ethanol plant and hydrolyzed sucrose from the sugar beet plant from the existing biorefinery in Pomacle, France. Production from this facility is expected to come online in the fall of 2009. Bioamber intends to license out its 1<sup>st</sup> turn-key solution packages in 2010 and claims that commercial-scale biobased succinic acid production will be reached in 2011/2012. In terms of what feedstock will be used – whichever sugar source is most economical – the company is taking a regional approach.

The company's development efforts are currently focusing on improving their current technology through yield improvements and through purification improvements, as well as developing direct fermentation routes to succinic acid derivatives. Recently, as of May of 2009, DNP announced a scientific agreement with the National Research Council of Canada Biotechnology Research Institute (NRC-BRI) to develop a second-generation microorganism for biobased succinic acid production.

#### **Roquette and DSM – SUCCINIUM Project**

Roquette and its partner DSM are also focused on commercializing a biobased succinic acid production process. Roquette and DSM have announced the SUCCINIUM project under the BioHub program. BioHub, which is subsidized by OSEO Innovation, is a development program of new cereal bio-refineries led by Roquette and seven other industrial partners: Arkema Chemists (France), DSM (Netherlands), Solvay (Belgium), Cognis (Germany), the road designer Eurovia (Vinci group), the company Sidel (specializes in bottling systems of polymers), and Tergal Industries (producer of polyethylene terephthalate). The SUCCINIUM project is related to the production of biosourced succinic acid by fermentation. Roquette has obtained rights to an E. coli strain developed by Rice University which claims a succinic acid yield close to maximum theoretical yields. Additionally, the company has licensed a succinic acid production technology using microorganisms from the University of Georgia. The company plans to have a demonstration plant in France of several hundred MT/yr operational by the end of 2009, and expects to reach large scale production by 2011/2012.

#### **BioEnergy International**

BioEnergy International, which has recently announced the formation of Myriant Technologies to house their biobased chemicals business and related intellectual property, has developed a biocatalyst to manufacture succinic acid. The company claims that its proprietary technology enables the derivation of five other DOE top 12 chemicals. According to the company's website, the company plans to begin commercial scale production of succinic acid in early 2010. However, according to 2008 company presentations, the technology appears to be 3-6 years away from commercialization. More detailed information was unavailable.

## **4. SWOT**

The following is a summary of the strengths, weaknesses, opportunities and threats to succinic acid technology development for the Minnesota corn industry.

**Table 20: SWOT – Succinic Acid**

<b><u>Strengths</u></b>	<b><u>Weaknesses</u></b>
<ul style="list-style-type: none"> <li>▪ Very large market potential</li> <li>▪ The process consumes CO<sub>2</sub></li> <li>▪ Green process that provides an alternative to petrochemicals</li> <li>▪ Economics are such that biobased succinic acid is close to being competitive with petrochemical alternatives when crude oil is ~\$65/barrel.</li> <li>▪ Fermenting microorganisms can utilize 5 carbon sugars as well as glucose.</li> </ul>	<ul style="list-style-type: none"> <li>▪ Not yet proven at a commercial scale → expected to approach commercial scale production in 2011/2012.</li> <li>▪ High downstream processing costs – purification and separation of succinic acid and process by-products.</li> <li>▪ Not all of the derivatives can be produced from succinic acid at a cost that is competitive with petrochemical alternatives</li> <li>▪ High capital cost requirements</li> <li>▪ Distance from traditional chemical industry – infrastructure, knowledgeable personnel, and potential investors.</li> <li>▪ Benefits from this technology are not limited to corn; other sugar feedstocks can also be utilized – will depend on regional economics.</li> </ul>



<u><b>Opportunities</b></u>	<u><b>Threats</b></u>
<ul style="list-style-type: none"> <li>▪ High crude oil prices</li> <li>▪ Ability to co-locate with current corn processing facilities, including ethanol plants.</li> <li>▪ First mover-advantage allows early market entrants the opportunity to capture premium prices in higher value-added markets.</li> <li>▪ Technology is at an early stage of commercialization with opportunities for process improvements.</li> <li>▪ A cap-and-trade system would improve process economics.</li> <li>▪ “Green product” marketability – may command small premium in niche markets</li> <li>▪ The development of cellulosic ethanol technologies can provide additional sugar streams for succinic acid production.</li> <li>▪ Biobased products could help meet LEED certification requirements.</li> <li>▪ Growing world demand for plastics and other biobased products.</li> <li>▪ Biobased products may qualify for the USDA BioPreferred program.</li> </ul>	<ul style="list-style-type: none"> <li>▪ Low crude oil prices</li> <li>▪ High feedstock costs</li> <li>▪ Tight capital markets</li> <li>▪ Favorable economic competitiveness of non-corn based succinic acid.</li> </ul>

## H.Zein Extraction

### 1. Product/Technology Overview

Various processes have been developed to extract zein protein from corn and corn by-products (e.g., DDGS). Zein is a high-value protein which can be used in a wide range of applications. Zein is not used extensively in human food products, despite being edible, due to its negative nitrogen balance and poor water solubility. However, this insolubility is what makes zein and its resins form tough, glossy, hydrophobic grease proof coatings that are resistant to microorganisms, heat and humidity.

Applications include:

- Specialty coatings for pharmaceutical tablets, candies, nuts, and paper products (e.g., glossy magazines) – serves as a water barrier
- Chewing gum
- Adhesives and binders
- Printing ink
- Cosmetics
- Fibers and textiles
- Paints and varnishes
- Resins and biodegradable plastics
- Edible moisture barrier on fruits and vegetables to extend shelf life
- Food coatings that reduce fat absorption
- Edible hay bale wrappers
- Used to mimic fat to replace 50-100% of the fat in mayonnaise, ice cream, and spreads.
- High-value bio-medical applications (e.g. tissue scaffolding used for skin regeneration). Because it is of plant origin and not animal, there is less concern of disease or virus issues. Only the high purity zein can be used for these applications.

Currently, zein can be extracted from corn gluten meal, a by-product of the wet milling process. However, current extraction and purification technologies are such that the price of zein limits current market applications. However, there are several technology companies/institutions currently working to lower extraction and purification costs.

Approximately 75% of the proteins in corn are found within the endosperm (portion of the corn kernel that contains the starch used to make ethanol), and zein is the main protein within corn, accounting for 40-50% of the total corn protein. The zein protein can be extracted from the corn prior to fermentation or from the resulting DDGS co-product. The different companies/institutions pursuing the development of zein extraction technologies have varying approaches as to whether it is more economical for the dry grind ethanol facility to extract the zein prior to fermentation

or from the DDGS at the back-end of the process. Each of their technologies and approaches are profiled in section IV.H.3.

In addition to zein extraction, most of these processes also extract corn oil, and some processes are integrated fractionation technologies which combine the zein extraction technology with other corn fractionation technologies, thus producing a whole suite of co-products, including corn oil, bran/fiber, zein proteins, and ethanol. The combined value of these products is higher than the value of the DDGS produced from a typical dry grind ethanol facility.

## 2. Market Potential

Zein is currently a high value product. According to zein extraction technology developer, Cheryan Munir of the University of Illinois, the current cost of purified zein is \$9-32/lb. Another technology developer based in the Netherlands quoted zein prices in a June 2009 presentation at \$4.54-18.14/lb, and a U.S. technology developer (Bio Process Innovations) is using a price of \$7/lb in its own economic analysis. All sources note that this price range depends largely on the purity of the zein protein, and that at these current prices, it is uneconomical for the use in many market applications, such as biodegradable plastics. Prices would likely come down toward the bottom end of the range if large-scale zein extraction at dry-mill began to take place.

However, current zein prices, even at the low end, provide significant economic incentive for technology developers to create an economically viable process that corn-to-ethanol facilities can use to extract zein from corn or from DDGS. According to Bio Process Innovations, the yield of zein proteins from their process is 0.8 lbs/bu. At a zein price of \$7/lb, an ethanol price of \$1.55/gal, and a ethanol yield of 2.7 gal/bu, the revenues from zein exceed that of ethanol, and most certainly compensate for any loss in DDGS revenue (see Table 21).

**Table 21: Comparison of Potential Zein, Ethanol, and DDGS Revenues**

Product	Price	Yield	Gross Revenue
Zein Protein*	7 \$/lb	0.8 lbs/bu	\$ 5.60
Ethanol	1.55 \$/gal	2.7 gal/bu	\$ 4.19
DDG	125 \$/ton	17 lbs/bu	\$ 1.06

\*Yield and price - Bio Process Innovations

The big question is cost. While a December 2008 article in *Ethanol Producer Magazine* stated that there is currently no cost-effective way to recover and purify zein protein, there are several companies and research institutions working to develop technologies to bring these extraction and purification costs down.

### 3. Profiles - Companies & Research Institutions

#### **University of Nebraska, Lincoln**

University of Nebraska, Lincoln has patented a process to extract and isolate zein and oil (if desired) from DDGS or corn using an acidic extraction solution. While either cereal grains or cereal grain by-products can be utilized, technology developers argue that using by-products is a less expensive production method. The zein obtained from this process is said to be suitable for fibers, films, and binders in paints. They also claim that their new acidic extraction technique improves the quality of the zein product.

#### **Purdue University**

Purdue University has patented a technology which uses alcohol to extract the zein and oil from the corn prior to fermentation. Then, the insoluble bran fiber and gluten meal are separated out before the remaining solution of starch and sugars is fermented into ethanol. Developers claim that the process uses 1/3 less water than traditional dry grind ethanol plants and produces no wastewater streams, while increasing ethanol yields and reducing throughput time. They also claim that the process reduces operational costs compared to a traditional ethanol plant.

#### **Prairie Gold / University of Illinois**

Prairie Gold is the developing and commercializing company for a corn oil and protein extraction process (COPE) developed by the University of Illinois which uses ethanol to extract oil and zein from corn prior to fermentation and then membrane technology to separate, isolate, and purify the zein. This membrane technology also allows for the recycling of the ethanol solvent without substantial evaporation losses, which currently limit other zein extraction processes. According to the extraction technology developer, Cheryan Munir, preliminary economic analysis shows a \$2-4/bu net income increase without any additional materials required (process requires corn and recyclable ethanol).

Prairie Gold claims that because the zein has not been exposed to the steeping chemicals and processing steps used in wet corn milling, where it can be extracted from corn gluten meal, it is in a more “natural” state and has better functionality for certain applications. The process can produce several grades of zein ranging from 50-90% protein (dry basis) and with varying amounts of color.

The company has formed collaborations with KATZEN, an ethanol plant technology and design company, to integrate the process into dry grind ethanol plants.

According to Munir, the insolubility of zein proteins limit their functionality in human food products. However, the University of Illinois has developed a unique two phase process involving an organic phase enzyme reaction followed by an aqueous phase enzyme reaction to improve the water solubility of zein proteins from 0-99%.

**USDA, ARS / Global Protein Products**

The USDA, ARS is also working to develop cost efficient methods to extract and purify zein from corn and corn by-products, as well as investigating new uses for zein. Recently, ARS researcher, David Sessa, has developed a cost effective method to purify zein. Global Protein Products, which currently sells zein protein products, plans to use this process, taking it from pilot to commercial scale. The company notes that there is industrial demand for the product.

Prior to this ARS process, activated carbons were used to bind and trap the compounds causing zein's color and odor (limiting its use in a variety of products, including biomedicines). However, this process results in a 37% to 95% loss in zein, thereby making purified zein very costly. ARS's process uses zeolites, silicate, or clay-based particles to act as molecular sieves, reducing loss to 25%.

**Iowa State University**

Iowa State University has evaluated aqueous ethanol, alkaline-ethanol, and aqueous enzyme treatment methods for extracting oil and protein from distillers grains. Study results indicated that enzymatic and alkaline-ethanol extraction methods were equally effective, while the basic alcohol extraction method was less effective.

**Zea Fuels**

Netherlands based Zea Fuels is working to improve small scale bioenergy solutions with their ethanol and biogas system that isolates zein proteins using a proprietary process. Lab studies indicate that their process can reduce the price of zein more than 400%, going from €5-45/kg to €1-5/kg.

**Bio Process Innovation, Inc**

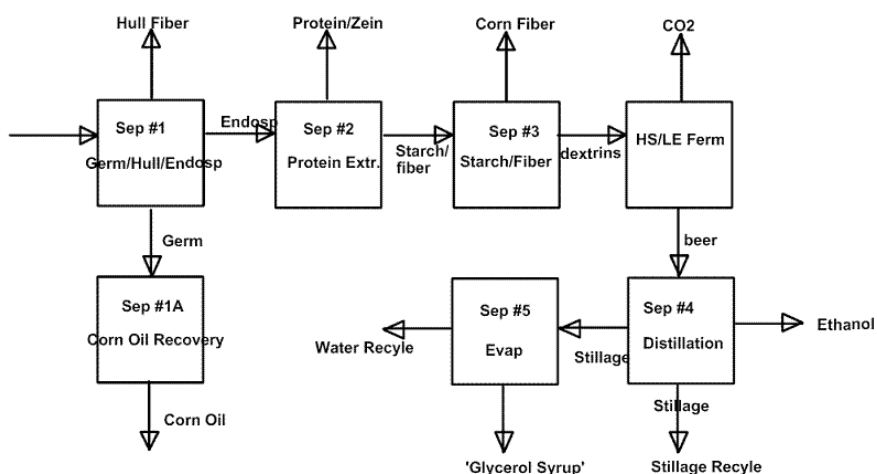
Bio Process Innovation, Inc (BPI) is marketing a technology they refer to as "High Value Corn" (HV Corn), whereby the corn germ is separated out using Cereal Process Technologies' front-end fractionation system and then extracted using a proprietary recovery system. Then, proprietary processes are used to extract the zein from the endosperm. In the end, their process produces six products: corn germ/oil, corn bran, zein proteins, nutritional proteins<sup>27</sup>, corn fiber, and ethanol. According to the company's website the HV Corn process increases gross sales by a factor of nearly 3.

BPI is currently working on two projects, one in Iowa and the other in Indiana. However, both are still in the capital raising stages.

Figure 23 illustrates the concept of the HV Corn process, integrated with other proprietary processes.

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<sup>27</sup> The residual non-soluble proteins that remain after extraction of zeins.

**Figure 23: Bio Processing Innovation's HV Corn Process**

Source: Bio Processing Innovations, Inc.

#### 4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to zein extraction technology development for the Minnesota corn industry.

**Table 22: SWOT – Zein Extraction**

<p style="text-align: center;"><b><u>Strengths</u></b></p> <ul style="list-style-type: none"> <li>▪ Moderate market potential             <ul style="list-style-type: none"> <li>○ Strong potential impact on ethanol margins, particularly for 1<sup>st</sup> movers</li> </ul> </li> <li>▪ Moderate institutional support</li> <li>▪ High zein prices</li> <li>▪ Some claim that the process reduces wastewater</li> <li>▪ Some claim that the process increases ethanol yields and reduces throughput time</li> </ul>	<p style="text-align: center;"><b><u>Weaknesses</u></b></p> <ul style="list-style-type: none"> <li>▪ Loss of distillers grains revenues</li> <li>▪ High purification costs</li> <li>▪ Current economic feasibility is questionable.</li> <li>▪ Not yet proven at a commercial scale</li> </ul>
<p style="text-align: center;"><b><u>Opportunities</u></b></p> <ul style="list-style-type: none"> <li>▪ Technology offers a potential advantage for existing ethanol producers – helps keep already existing infrastructure investments profitable.</li> <li>▪ First mover-advantage allows early market entrants the opportunity to capture premium prices in higher value-added markets.</li> <li>▪ Technology is at an early stage of commercialization with opportunities for process improvements</li> <li>▪ Risk mitigation             <ul style="list-style-type: none"> <li>○ More than two revenue sources</li> <li>○ Increased flexibility</li> </ul> </li> <li>▪ Development of front-end fractionation technology.</li> <li>▪ Could help provide an alternative use of distillers grains, particularly as distillers grains markets become saturated.</li> <li>▪ “Green product” marketability</li> <li>▪ Biobased products could help meet LEED certification requirements.</li> <li>▪ Growing world demand for plastics and other biobased products.</li> <li>▪ Biobased products may qualify for the USDA BioPreferred program.</li> <li>▪ If the EPA grants an allowance for an ethanol blending rate of up to 15%, this will facilitate an increase in ethanol production.</li> </ul>	<p style="text-align: center;"><b><u>Threats</u></b></p> <ul style="list-style-type: none"> <li>▪ Tight capital markets</li> <li>▪ If the EPA does not grant an allowance for an ethanol blending rate of up to 15%, ethanol production volumes will be constrained by the current 10% “blend wall.”</li> <li>▪ If a number of ethanol facilities incorporated the technology, zein values will decrease.</li> </ul>



## Appendix A: Phase I – Corn Products/Technologies

Initially, more than 100 “emerging” corn products and/or technologies were identified. This appendix lists the products/technologies which were each reviewed based on their demand/market potential, economic feasibility, stage of development, and strength of institutional support. While Informa attempted to be as complete and as accurate as possible in its evaluation of each of these products/technologies, it is acknowledged that given the lack of perfect information about all four assessment criteria for all 100+ products and technologies, some products and/or technologies may have been under/over estimated. However, through interviews with industry experts, confirmation was given to final selections.





Products/technologies presented within this section are grouped into the following categories:

- Improving Current Ethanol Production Economics
- Second Generation Biofuels
- Value-Added Chemicals from Sugars
- New Uses of Corn Cobs
- New Uses of Distillers Grains
- New Uses of CO<sub>2</sub>
- Lignin Derived Products
- Other New Corn Uses/Products
- New Corn Varieties Designed for Non-Fuel Applications




It is noted that some products/technologies may apply to more than one category, yet they are only listed once. For example, some of the technologies listed under “Improving Current Ethanol Production Economics” may also be applied to cellulosic ethanol production processes; new uses of distillers grains and new uses of CO<sub>2</sub> can also be considered technologies under “Improving Current Ethanol Production Economics”; lignin derived products could also be classified as cellulosic ethanol technologies; and butanol is listed under second generation biofuels, but is also a “Value-Added Chemical from Sugar”.






Note that the stage of development was divided into four distinct phases as shown in Table 23.





**Table 23: Development Stage**





Well Established	Initial Commercialization	Early Development Stage	Research/Conceptual Stage
			

**Table 24: Improving Current Ethanol Production Economics**

Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
<b>Feed Stock Preparation Technologies (Milling, Liquefaction, and Saccharification)</b>			
<b>Static, Hydrodynamic Cavitation</b>	A patented process designed to improve ethanol processing efficiency and yield. The goal is to improve starch recovery by 2-5%. Grain and liquid medium flows through a controlled flow cavitation apparatus at a velocity capable of generating a hydrodynamic cavitation zone where the grain size can be reduced. Powerful cavitation forces fracture the particles, resulting in high surface area dispersions. This high surface area causes faster hydrolysis from starch to sugar. This is a continuous flow process which any ethanol facility can be retrofitted to include. Company claims include: high throughput, accelerated reaction times; high capacity, small footprint system and simplicity of design; scalable system; energy-savings; high conversion efficiency; and lower capital, maintenance, and spare part costs.	- Arisdyne Systems, Inc. (Controlled Flow Cavitation™) - Delta-T	
<b>Ethanol Reactor Tower</b>	The ethanol reactor tower (ERT) is positioned next to the liquefaction tank so that the slurry passes through the ERT prior to liquefaction. Highly atomized steam is used to cause cell disruption and to activate more starch. This decreases liquefaction time and heat, reduces amylase requirements by 20-50%, and ultimately produces a reported 10% higher ethanol yield. The company claims that the technology could amount to a \$500,000 a year savings.	- Pursuit Dynamics	
<b>Ultrasonic Process</b>	The ultrasonic technology is applied to the cooked corn slurry, resulting in a more efficient breakdown of starch and ultimately higher ethanol yields.	- FCStone Carbon LLC - Iowa State University	






Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
<b>Enzyme Development</b>	Research is ongoing to find and develop enzymes for liquefaction and saccharification with similar optimal temperature and pH requirements, so as to reduce the cost and time currently associated with having to make temperature and pH adjustments between the liquefaction step and the saccharification step, where optimal pH and temperatures differ between amylase and glucoamylase.	- National Research Laboratory for Functional Food Carbohydrate and Center for Agricultural Biomaterials - Seoul National University	
<b>Granular Starch Hydrolyzing Enzymes (GSHE)</b>	GSHEs help ferment starch even when it is still crystalline in nature and reduces the use of heat in the dry grind process. Converts the starch without the "cooking" step, thus reducing energy consumption. May also result in higher ethanol yields, reduces microbial contamination, and lowers enzyme requirements.	- University of Illinois - POET (BPX™ Process) - Genencor (Stargen) - Novozymes	
<b>Fermentation Technologies</b>			
<b>High Speed/Low Effluent Process</b>	A patented process that allows near complete fermentation of 18-25% glucose to ethanol in 4-10 hours in continuous cascade or consecutive batch mode over extended periods of several to many months. Bio Process Innovation claims that the process increases the productivity of fermenters by a factor of 6-10 times without resorting to centrifugal cell recycling, it decreases effluent stillage by using a high degree of backset, decreases nutrient needs/costs, produces a clean 'beer' to take to the distillation column, produces a clean, high density yeast paste by-product with no need for centrifuges, reduces waste water/cleaning chemicals by eliminating the need for "cleaning in place" (CIP) of fermenters between batches, reduces operator/lab labor as the process is easily automated, and eliminates the need for yeast purchase/propagation.	- Bio Process Innovation, Inc	
<b>High Gravity Fermentation</b>	An experimental technology that would allow for higher ethanol concentrations during the fermentation process by using a highly concentrated mash. This process would lower the water required in the ethanol production process (up to 59%), which in turn reduces energy costs by 4% (Belcher, 2005), as there is less fluid to heat, cool and distill. Additionally the process would increase plant throughput. Tests have shown increased fermentation yields, but challenges still exist in overcoming tolerance issues.	- University, Tirupati, India - University of Sheffield, UK - Technical University of Denmark - Novozymes - University of Saskatchewan	
<b>Yeast/Bacteria Developments</b>			
<b>More Tolerant Yeast</b>	Research is ongoing to find or develop yeast strains with improved tolerance to higher temperatures, ethanol, and osmotic pressure. This would allow for faster throughput via faster reaction times and higher ethanol concentrations (limiting the toxicity issue). It would also reduce contamination issues. However, higher temperatures mean increased energy use and increased ethanol vaporization.	- Massachusetts Institute of Technology - Berlin University of Technology - Whitehead Institute for Biomedical Research	

Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
Arabinose Yeast	NREL is working on designing unique biocatalysts to ferment arabinose, a major component in the available sugars from corn fiber, a residue of the corn-to-ethanol process, into ethanol. Research in ongoing to find a thermophilic (heat loving) bacteria to ferment the sugars rather than a yeast. This would allow for fermentation to occur at higher temperatures which would increase plant throughput through faster reaction time. One benefit of bacteria over yeast is that it is easier to genetically manipulate. However, there are several drawbacks of using bacteria, including increased by-product production, higher pH requirements, limited range of acceptable feed sugars, and low ethanol concentrations. There are several bacteria strains that have been considered, each with their own advantages and disadvantages.	- NREL - NCGA - Corn Refiners Association	
Thermophilic Bacteria	Low temperature fermentation results in lower energy usage and lower ethanol evaporation; however, with the lower temperatures, reaction times are slower and there is increased bacterial contamination. While these pros and cons must be weighed against one another, there are research efforts ongoing to develop "cold loving" yeast strains with improved performance in cold conditions over traditionally used yeast strains.	- Dartmouth College	
Lower Temperature Fermentation - Yeast	Rather than using freely suspended yeast cells, "yeast immobilization" refers to the use of immobilized cell reactors to constrain the volume of yeast to a defined volume, typically imbedded or bound to a solid support structure. These immobilized cell structures eliminate cell washout and the need for cell recycle, increases productivity as there is no constraint on feed flow rates, and allows for better overall control over the microbial environment. However, there are still several disadvantages, including mass transfer limitations which may slow cell metabolisms and reaction kinetics, and damage to the support structure can occur over time.	- Universitat Rovira i Virgili (Spain)	
Yeast Immobilization	One of the challenges facing both corn-based ethanol and cellulosic ethanol producers is that while the fermenting agent is producing ethanol, other unwanted acid by-products are also being produced which are difficult to separate out of the mixture. These contaminants also compete with the yeast for vital nutrients and decrease ethanol production efficiency. Traditionally, antibiotics are used to control contaminating bacteria; however, there is rising concern over the use of antibiotics and the resulting presence of residual material in distillers grains, not to mention the cost of these antibiotics. However, there are several novel alternatives to dealing with this contaminating bacteria issue.	- University of Melbourne (Australia) - Chinese Academy of Sciences - Universiti Sains Malaysia	
Contaminant Bacteria Reduction		(see below)	(see below)





Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
Inhibitory Organisms Detection Kit	This detection kit is designed to detect the presence of the acid-producing bacteria and yeast within the ethanol production process that produce acids such as lactic acid and acetic acid. These acids compete with the ethanol producing yeast <i>Saccharomyces cerevisiae</i> for vital nutrients, which in turn inhibit ethanol yields. This technology is different from the standard detection technology often used in the industry which only detects the acids themselves. This detection technology allows ethanol producers to take proactive measures to prevent the formation of these harmful acids.	- ETS Laboratories (Scorpions)	
Reactive Distillation	While inorganic catalysts have long been known as a method to produce valuable chemicals in the petroleum industry, its application on corn-based feed streams has been cost prohibitive due to challenges associated with separating the mixture of chemicals that are derived from a feed stream with multiple compounds. However, the "reactive distillation" process separates a mixed stream of different chemicals by treating that stream with a reactive chemical in the presence of a catalyst.  This technology is designed to separate out these acids from the ethanol. This would allow an ethanol or cellulosic ethanol facility to be a biorefinery, producing more than just ethanol. For example, MSU researchers are currently focusing on the production of ethyl lactate from lactic acid.	- Michigan State University - National Corn Growers Association	
Hops (Contaminating Bacteria Reduction)	Recently, it has been shown that the natural acids of hops will stop the growth of certain contaminating bacteria well enough to avoid the use of antibiotics.	- BetaTec Hop Products - Universität Hohenheim Institut for Food Technology	
<b>Distillation Technologies</b>			
<b>Alternative Ethanol Distillation Technologies</b>	The separation of alcohol and water is typically a costly, energy intensive process, representing a significant portion of the overall energy use required by an ethanol facility. Traditionally, this separation is performed through a combination of steam distillation and a molecular sieve. However, there are various processes being developed whereby ethanol is removed during fermentation, reducing product inhibition and energy costs, and thereby also decreasing greenhouse gas emissions.	(see below)	
Vacuum Stripping	The fermenting vessel is coupled with a vacuum chamber which extracts, in-situ, the more volatile ethanol and allows for partial product removal.	- University of Illinois	













Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
Gas Stripping	The fermenting broth overflowing from one stage to the next is contacted with a CO <sub>2</sub> stream that entraps the ethanol. The ethanol is then removed when this gas stream passes across a reactor and through an absorption tower where it is contacted with water. The CO <sub>2</sub> is then re-circulated. By using this process, the concentration of sugar in the product stream entering the fermenter is increased.	- Bio-Process Innovation, Inc	
Solvent (Liquid) Extraction	This approach removes the product that causes inhibition through an extractive biocompatible solvent that favors the migration of ethanol to solvent phase, a process known as extractive fermentation. However, it has been noted in one publication that this approach lowers solubility and results in a poisonous effect on yeast, thus restricting the development of this method.		
Membrane Separation	Membranes are used to filter the water/ethanol mixture during fermentation. The membranes are vapor phase separation units that allow the preferred permeation of water over other vapor components in a gas mixture.	- Vaperma (Siftek) - Whitefox Technologies Limited	
Esep	"ESeP is a modular, low-energy process for the recovery of ethanol from fermentation broth with an estimated reduction of up to 60% in both capital and operating costs versus conventional distillation. Use of non-stainless steel components also results in a substantial reduction in construction time". While a 60% reduction in energy consumption is estimated when incorporating the system into new ethanol and cellulosic ethanol plants, a 28% energy reduction and a 16 month payback period is estimated when retrofitting and existing ethanol plant.	- Trans Ionics Corp. (Esep)	
Supercritical Fluids	While the success of separating alcohol and water via supercritical fluids has been demonstrated for many years, these previous demonstrations have not been able to compete with the economics of traditional steam distillation methods or other proposed methods such as membrane separation. However, MOR Supercritical has applied their supercritical extraction technology ethanol dehydration, and claims a process that is scalable and cost-efficient relative to other proposed dehydration technologies.	- MOR Supercritical, LLC	
Low Energy Distillation Technology	A commercially demonstrated process whereby the concentration of 96% ethanol is allowed without the use of thermal energy, saving the facility in energy costs. The process uses "specially designed columns, packing, condensers, and reboilers to replace 12-15 lbs of steam required in distillation of a gallon of ethanol with 0.3 KW of electricity." The company claims that this process could save a 10 MMGY ethanol plant \$2-\$4 million a year.	- Liqua Ethanol	

Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
<b>Co-Product Technologies</b>			
<b>Enhancing Water Removal from Whole Stillage by Enzymes</b>	The addition of cell-wall-degrading enzymes are added to the ethanol production process in order to reduce the amount of water bound within the wet grains. This allows for more water to be removed during centrifugation, reducing the time and energy required to dry the distillers grains. GlycosBio has developed microorganisms that make high-value chemicals from lower valued co-product streams of existing industries, such as thin stillage from ethanol.	<ul style="list-style-type: none"> <li>- USDA, ARS</li> <li>- Washington University, St. Louis</li> </ul>	
<b>GlycosBio</b>		<ul style="list-style-type: none"> <li>- GlycosBio</li> <li>- Rice University (original technology developer)</li> </ul>	
<b>Fungus Removal of Organic Material and Solids from Thin Stillage</b>	Researchers have added a fungus to the thin stillage by-product of ethanol production. This fungus removes about 80% of the organic material and all of the solids, allowing the water and enzymes to be recycled. The remaining fungi can potentially be used as a high value feed supplement. Normally, because the solids can interfere with ethanol production, only about 50% of the thin stillage can be recycled back into the ethanol process, while the rest is evaporated and blended with the dried distillers grains. Researchers say that this process could reduce energy costs by as much as a third. It also reduces water consumption and saves producers enzyme costs.	<ul style="list-style-type: none"> <li>- University of Hawaii</li> <li>- Iowa State University</li> <li>- MycolInnovations Inc (MycMax)</li> </ul>	
<b>Anaerobic Digestion</b>	Anaerobic digestion uses bacteria to convert the thin or whole stillage by-product of ethanol production into biogas – a mixture of methane (50-70%), CO2 (30-50%), and trace amounts of H2, NH3, and H2S, which can then be used to reduce natural gas usage. This process reduces energy costs and greenhouse gas emissions and helps to conserve water.	<ul style="list-style-type: none"> <li>- Washington University</li> <li>- University of Minnesota</li> <li>- USDA, ARS</li> <li>- Iowa State University</li> <li>- Rein &amp; Associates (MN)</li> <li>- Biogasol</li> <li>- POET</li> <li>- University of Borås</li> <li>- Kwartha Ethanol</li> </ul>	
<b>Microwave Drying of Distillers Grains</b>	Microwave drying technology is an alternative to conventional rotary drum gas dryers used to dry the animal feed co-product. This process uses industrial drying systems to dry and treat the feed co-product. While the microwave energy breaks down the structure of the cell walls, Cellencor's patented enzymes increase the value of the by-product feed, increasing the available energy of the feed. The process uses less energy than traditional dryers, reduces greenhouse gas emissions, improves water reclamations, and enhances the value of the animal feed co-product. This process has been field tested at both dry and wet mill ethanol facilities. The company claims that the process could save ethanol producers 20% or more in operating costs. The payback period for the technology was estimated to be 2-5 years (estimated in 2008).	<ul style="list-style-type: none"> <li>- Cellencor- Corn Plus-Kwartha Ethanol</li> </ul>	



Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
<b>Acetic Acid - Produced from Bottoms Fraction of Ethanol Distillation</b>	A patented process designed to increase ethanol yield by taking the bottoms fraction from ethanol distillation, and through a combination of biochemical and synthetic conversion processes, produces acetic acid. Acetic acid can then be converted into ethanol using esterification and hydrogenation reactions.	- Zechem, Inc.	
<b>Fractionation and Extraction Technologies</b>			
<b>Front-End Fractionation</b>	There are several modified dry-mill front-end fractionation processes that separate the corn entering into the ethanol facility into three fractions: pericarp (bran/fiber), germ, and endosperm. The germ is the oil-bearing portion of the kernel. Revenue streams generated from this process include corn oil; high protein, low fat and fiber distillers grains; fiber and ethanol. Additionally, front-end fractionation allows for more efficient starch fermentation as non-fermentable products are no longer taking up valuable space in the fermenters, yet there is also some level of starch loss during fractionation. According to some technology developer claims, front-end fractionation can also reduce energy consumption and lower volatile organic compound emissions.	(see below)	(see below)
Modified Dry Grind Wet Fractionation	Wet fractionation technologies typically involve soaking/steeping the corn prior to fractionation. In general, the costs are higher than that of dry fractionation technologies, but the starch loss is lower and the quality of co-products is higher.	<ul style="list-style-type: none"> <li>- Maize Processing Innovators &amp; FCStone Carbon LLC (Quick Germ Quick Fiber)</li> <li>- Corn Value Products (HydroMilling™)</li> <li>- University of Illinois (E-Mill)</li> </ul>	
Modified Dry Grind Dry Fractionation	Dry fractionation technologies typically separate the germ and fiber from the corn kernel mechanically without the need for soaking. In general, the costs are lower than that of wet fractionation technologies, but the starch loss is higher and the quality of co-products is lower	<ul style="list-style-type: none"> <li>- University of Illinois (Dry Degerm Defiber Process)</li> <li>- Renessen LLC. (Extrax™ Processing System)</li> <li>- Delta-T/Ocirm (Dry Separation Technology™)</li> <li>- Poet / Satake Corp. (BFRAC™ Process)</li> <li>- Crown Iron Works (Crown Fractionation System)</li> <li>- Cereal Process Technologies</li> </ul>	
MOR-Frac™ Plus* (Dry Fractionation, Wet-Mill Germ)	A "second generation fractionation" process with the product separation and co-product quality advantages of wet fractionation technologies (expected to generate less than 2% starch loss, germ oil yield is 40%-45% and crude protein of DDGS is > 58%) with lower capital and operating costs, closer to that of a dry fractionation technology.	- MOR Technologies (MOR-Frac™ Plus*)	





Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
<b>Corn Oil Extraction/Separation (Front-End)</b>	Processes whereby the corn oil is separated from the corn germ prior to fermentation.	(see below)	(see below)
Aqueous Enzymatic Extraction	An alternative oil extraction technology that does not use hexane or other hazardous solvents. This process uses an aqueous enzymatic oil extraction technology to separate the oil from enzymatically wet milled corn germ. Developers claim oil yields of 70-90%.	- USDA, ARS (Amazing Oil)	
Supercritical Carbon Dioxide Corn Oil Extraction	This system can also be coupled with MOR Technology's fractionation system (MOR-FRAC Plus+) to provide added value for ethanol facilities or as a stand alone facility to produce high quality, specialty oils, bioactive ingredients, or nutraceuticals. Rather than using hexane, MOR Supercritical's technology uses carbon dioxide as their only solvent in their corn oil and oilseed extraction system. As opposed to conventional supercritical processes, MOR Supercritical claims that their technology greatly reduces operating costs which have prevented other supercritical systems from replacing petrochemical extraction using hexane. MOR Supercritical claims that their technology is energy efficient; automated, modular and scalable; has a small environmental footprint (1/6 of a typical solvent extraction plant); produces safe, solvent-free, non-degraded, high-quality products including undegraded meal with high protein digestibility; and an accompanying refining technology to extract and refine the oil in one step.	- MOR Supercritical, LLC	
<b>Zein Extraction</b>	Various processes have been developed to extract zein protein from corn and corn by-products (DDGS). While most of these processes focus on extracting the zein prior to fermentation others concentrate on extracting the high-value protein from the back-end. In addition to zein extraction most of these processes also extract corn oil and some processes are further integrated fractionation technologies which separate out products such as bran and fiber. Zein is a high-value protein which can be used in a wide range of applications, including: specialty coatings for pharmaceutical tablets, candies, and paper products; chewing gum, adhesives and binders; resins and bio-plastics; printing ink; cosmetics; and high-value bio-medical applications. The purer the zein, the more high value food and pharmaceutical applications it can be used in.	- Prairie Gold (COPE) - University of Illinois - KATZEN - Purdue University - Bio Process Innovation, Inc - University of Nebraska - USDA, ARS - Global Protein Products - Iowa State University - Zea Fuels (Netherlands)	
<b>Protein Separation - Chromatography</b>	A method used to extract high-value protein from raw material, which can be used in the production of food additives and ingredients and in the healthcare industry. The process is already being used at industrial scale in the potato industry and at a large dairy cooperative in Australia that processes cheese whey. The company has been talking with corn processors and ethanol producers to explore the possibility of implementing this technology in these industries.	- Upfront Chromatography (Rhobust)	







Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
<b>Elusieve Process (back-end fiber recovery)</b>	Process to recover the pericarp fiber at the back end of the dry grind process. Process involves elutriation and sieving, reducing the problem of using solely elutriation, a processes whereby non-fiber particles also get removed. This new process results in low fiber, high fat DDGS and a fiber co-product.	- University of Illinois (Elusieve Process) - USDA, ARS	
<b>Corn Oil Extraction (back-end)</b>	Basic corn oil extraction technology involves a centrifuge process to separate the oils from the corn stillage. By removing the oil from the distillers grains, the ethanol facility not only captures an additional revenue stream from the extracted corn oil, but also reduces their distillers grains drying costs and potentially greenhouse gas emissions. However, in comparison to front-end oil extraction processes, the oil extracted from the back-end is a lower-value product, as it cannot be used in food applications.	- GreenShift/Veridium (Corn Oil Extraction Systems) - Primafuel (SMAART Oil) - Iowa State University	
<b>Corn Fiber Fractionation</b>	This collaborative public/private partnership was formed to create high value products from corn fiber. They have developed a process by which a fiber stream is fractionated into its primary components: carbohydrates, oils, and proteins. The glucose within the carbohydrate fraction can be used to make ethanol/butanol and the other sugars can be catalytically converted to propylene glycol and ethylene glycol. In addition to capturing the 3% of the fiber fraction which is oil, the process also recovers the small oil fraction (5-25% of fiber oil) which is phytosterols. This small oil fraction has high value applications in the nutraceuticals markets and in the botanical oils market for personal care products. The remaining protein can then be used as a high value feed.	- National Corn Growers Association - Archer Daniels Midland Company - Pacific Northwest National Laboratory	Current status is unknown
<b>New Corn Varieties Designed for Ethanol Applications</b>			
<b>High Amylase Corn</b>	Using 3% amylase corn and 97% dent corn eliminates the need to add additional amylase to the ethanol production process. Syngenta estimates technology could cut production costs by 10%.	- Syngenta	
<b>High Total Fermentable Ethanol Hybrid Corn</b>	Corn that contains higher levels of fermentable starch, designed to improve ethanol yields. Many hybrids also contain Herculex® I insect protection which helps reduce the presence of mold and mycotoxins.	- Pioneer	
<b>Extrax Corn</b>	Monsanto is in the fourth and final stage prior to product launch of their high oil corn (7% compared to 3.5%) for use in Renessen's (JV between Monsanto and Cargill) Extrax corn fractionation system. They are focusing on higher oil content as this is the most valuable fraction of the corn.	- Monsanto	
<b>High Available Energy</b>	Hybrids with above average digestible energy for increased feeding value in swine and poultry diets. Helps to improve the value of the DDGS by-product.	- Pioneer	

Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
<b>Mavera™ High Value Corn with Lysine</b>	Corn with higher levels of lysine. Reduces the need for lysine supplements in swine and poultry diets. Helps to improve the value of the DDGS by-product, which has a low lysine content compared to other protein sources such as soybean meal.	- Renessen LLC. (JV: Cargill and Monsanto)	



<sup>1/</sup> Not an exhaustive list



**Table 25: Second Generation Biofuels**

Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
<b>Cellulosic Ethanol – Biochemical Platform</b>	Process to produce ethanol from corn biomass using biological agents to ferment the biomass, including corn kernel, corn stover, and/or corn cobs.		
<b>Pretreatment, Hydrolysis, and Fermentation Process Developments</b>	While there are many technologies and processes being developed to support economical cellulosic ethanol production, the base of the technology rests on pretreatment, hydrolysis, and fermentation.		
Pretreatments	The pretreatment of biomass is currently one of the single largest cost components in the overall cellulosic ethanol production process via the biochemical platform. Pretreatment is necessary in order to open up the structure of the biomass sufficiently to allow for effective hydrolysis. The protective sheath of lignin and hemicellulose must be removed or opened up so that the cellulose sugars are made accessible to be hydrolyzed, broken down into 5-carbon (C5) and 6-carbon (C6) sugars. There are many pretreatment methods currently being developed by numerous companies and research institutions, each with their own advantages and disadvantages. However, the bottom line is that a cost efficient process has yet to be commercialized.		 <sup>a</sup>
El Membrane Process	A process using DuPont's Nafion perfluorosulfonic membrane to recover the alkaline catalyst used in the cellulosic biofuel digesters during the pretreatment stage.	- Electrosep Inc.	
Combined Pretreatment and Hydrolysis Enzymes	Some of the more advanced pretreatments are done under conditions that would be amenable to enzyme stability and activity. This would enable the possibility of incorporating hydrolyzing enzymes into pretreatment stages, thereby combining the pretreatment and hydrolysis stages of cellulosic ethanol production.	- NREL	


Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
Hydrolysis	Hydrolysis converts the cellulose and hemicellulose to C5 and C6 sugars so that they can subsequently undergo fermentation.		
Fermenting Yeast/ Microorganisms	Researchers and technology companies are aiming to develop fermenting yeast/microorganisms that can efficiently utilize both the C5 and C6 sugars, thus increasing overall ethanol yields. Developments in this area are also looking to lower the required dosage of the fermenting agent and to increase their tolerance to fermenting conditions.	<ul style="list-style-type: none"> <li>- BP Energy Biosciences Institute</li> <li>- NREL</li> <li>- BioGasol</li> <li>- Mascoma</li> <li>- Dartmouth</li> <li>- DSM</li> <li>- Genencor</li> <li>- Novozymes</li> <li>- Verenum</li> <li>- Sandia National Laboratory</li> <li>- Abengoa Bioenergy New Technologies</li> </ul>	
Combined Hydrolysis and Fermentation	Development of a “cocktail” of enzymes that can both break down the cellulose and hemicellulose into C5 and C6 sugars and ferment them in a single step. Such a process is often referred to as consolidated bioprocessing.	<ul style="list-style-type: none"> <li>- Qteros</li> <li>- Mascoma</li> </ul>	
Sequential Hydrolysis and Fermentation (SHF)	As opposed to the simultaneous saccharification and fermentation process whereby the cellulase enzymes and the fermenting microbes are combined in one vessel, this process separates the hydrolysis step from the fermenting step. This enables the hydrolyzing enzymes to operate under their optimal temperatures and the fermenting microbes to operate under their optimal temperatures, thus increasing the overall utilization of the sugars.		
Continuous Reactor Separator (CRS) System	A system designed for combined hydrolysis, fermentation and separation of ethanol. The technology company claims that the process increases conversion rates, lowers energy usage during distillation, and efficiently recycles nutrients, chemicals and enzymes.	<ul style="list-style-type: none"> <li>- Liqua Ethanol</li> </ul>	
Triple-Crop Sugar Corn	A hybrid corn variety with high sugar-filled stalks, low grain yields, but high biomass yields - yields that beat record switchgrass yields for the Midwest. Also, this variety requires less nitrogen than grain corn varieties. The hybrid is a cross between popular U.S. lines and a tropical line. It would be similar to sweet sorghum but Bt and Roundup Ready versions could be applied, whereas biotech traits have not yet been developed for sorghum.	<ul style="list-style-type: none"> <li>- University of Illinois</li> </ul>	



Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
<b>Altered Plant Genetics - Self Degrading Biomass</b>	Novel varieties of corn whereby the cellulosic biomass begins to break down after harvest; reducing/eliminating the need for costly pretreatments.		
	A gene from the bacterium of a cow's stomach is inserted into a corn plant so that it can more easily convert the fiber in the corn stalks and leaves into simple sugars.	- Michigan State University (tech developer) - Edenspace Systems (holds license to tech) - (Energy Corn	
	Makes the plant's cell wall sugars more easily converted to biofuel. The company claims that the cell-wall sugars are more than twice as accessible to enzymatic digestion.	- Performance Plants (Efficient Conversion Trait)	
	Scientists have engineered novel "on/off" protein switches that are used to activate an enzyme within the plant cell wall that will begin to degrade cellulose into sugars after harvest. This enables the cellulosic biomass to be broken down at the cellulosic refinery using less severe pretreatments and without the addition of exogenous enzymes, resulting in a cost savings at the processing level.	- Agrivida (GreenGenes™) - Codon Devices (utilizes their BioLOGIC™ Engineering Platform) - University of Illinois	
<b>Hydrocarbon Mixtures</b>	Hydrocarbon mixtures can be used to produce a range of fuels and chemicals. Hydrocarbon fuels are virtually indistinguishable from gasoline, diesel, and jet fuel; can be distributed in existing pipeline infrastructure and can be used in any existing vehicle.		
<b>Microbial Conversion of Sugars to Hydrocarbons</b>	Custom deigned microbes convert sugars into hydrocarbon based fuels and chemicals.	- LS9 (DesignerBiofuels™) - Amyris - University of California, Los Angeles - University of California, Berkeley	 b

Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
<b>Thermochemical Platform</b>	<p>Pyrolysis/gasification technologies are used to produce a pyrolysis oil/syngas, from which a wide range of long carbon chain biofuels and chemicals can be reformed. In contrast to the biochemical platform, the thermo chemical platform is largely based on existing technologies and there appears to be fewer technical hurdles; although being a more mature technology there may be less opportunity for cost reductions. Research and development efforts are focusing on perfecting the gasification of biomass so that it is more reliable and cost efficient. One of the major technical challenges is that much of the syngas produced from biomass tends to be more heterogeneous than gas-based syngas, leading to variations in product quality. Also, the number of inhibitory substances vary by biomass feedstock and gasifier design. This variation in syngas composition creates problems for the Fischer-Tropsch process which creates a variety of chemical and fuel products from the syngas. Problems include low product selectivity and unavoidable co-products, as well as contaminants that can inhibit the catalytic reaction. Additionally, the large quantity of biomass required to reach a scale where the process is economical remains a concern.</p> <p>The Bioforming™ process combines the utility of aqueous phase reforming with catalysts and reactor systems similar to those found in traditional petroleum refineries to convert plant sugars into hydrocarbon mixtures that can be used to make a variety of conventional fuels (e.g., gasoline, jet fuel, diesel). The system is a catalytic, low-temperature thermochemical route to biofuel production.</p>	<ul style="list-style-type: none"> <li>- ALICO</li> <li>- Range Fuels</li> <li>- Flambeau LLC</li> <li>- New Page Corp.</li> <li>- Neste Oil</li> <li>- Stora Enso</li> </ul>	
<b>Bioforming</b>	<p>The Bioforming™ process combines the utility of aqueous phase reforming with catalysts and reactor systems similar to those found in traditional petroleum refineries to convert plant sugars into hydrocarbon mixtures that can be used to make a variety of conventional fuels (e.g., gasoline, jet fuel, diesel). The system is a catalytic, low-temperature thermochemical route to biofuel production.</p>	<ul style="list-style-type: none"> <li>- Virent Energy Systems (BioForming)</li> <li>- Royal Dutch Shell</li> <li>- Cargill and Honda Motor (Virent Investors)</li> </ul>	



Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved <sup>1</sup> (Technology Name)	Stage of Development
<b>Other</b>	Butanol is currently produced via petrochemical feedstocks and has the potential to be used in a wide array of applications, including: fuel, solvents, coatings (e.g., paint, varnish, and inks), agricultural chemicals (e.g., insecticides and herbicides), synthetic resins and adhesives, textiles (e.g., scatter rugs, bathmats), and sealants. As a fuel, butanol holds several key advantages over ethanol, including a higher energy content as well as its ability to be transported via pipeline.	<ul style="list-style-type: none"> <li>- BP and DuPont</li> <li>- Butyl Fuel LLC</li> <li>- TetraVita BioScience</li> <li>- Gevo</li> <li>- Cobalt Biofuels</li> <li>- Green Biologics</li> <li>- Syntec</li> <li>- METabolic Explorer</li> <li>- University of Illinois</li> <li>- University of California</li> <li>- Caltech</li> <li>- Ohio State University</li> <li>- Research Foundation</li> <li>- Joint BioEnergy Institute</li> <li>- USDA, ARS</li> </ul>	
<b>Butanol</b>	Over the past 20 years, research and development efforts have focused on improving various aspects of the acetone butanol, ethanol (ABE) production process. Molecular biology research has focused on developing various microbial strains with improved tolerance to butanol toxicity, which has resulted in significant yield increases. In 1990, the bacterium <i>Clostridium beijerinckii</i> was developed by Hans Blaschek from the University of Illinois, doubling butanol production over its parent strain, <i>Clostridium acetobutylicum</i> . Additionally, the development and application of in-situ gas stripping to remove the solvent from the fermenter, which minimizes product inhibition (the problem whereby the butanol becomes toxic to the fermenting agent), has enabled much higher feed concentrations.		

\* Red = Identified by the Consortium for Applied Fundamentals Innovation (CAFI)


1/ Not an exhaustive list




a/ Different pretreatment processes are at different stages of development. However, while some are currently being used in pilot and demonstration scale facilities, the pretreatment process remains one of the more costly steps in the overall cellulosic ethanol production process.


b/ Both LS9 and Amyris have announced plans to reach commercial scale production by 2011. However, both are focusing on using sugarcane from Brazil.



**Table 26: Value-Added Chemicals from Sugars**



\* Red = DOE Top 12 Value-Added Chemicals from Sugars and Syngas

Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>1,4-Diacids (Succinic, Fumaric, and Malic)</b>					
<b>Succinic Acid (SA)</b>	- 1,4-Butanediol (BDO) - Tetrahydrofuran (THF) - γ-Butyrolactone (GBL) - 2-Pyrrolidinone - N-Methyl Pyrrolidone (NMP) - Polytetramethylene Glycol (PTMG) - Poly-Butylene Succinate (PBS) - Diethyl and Dimethyl Succinate (Succinic Acid + Ethanol/Methanol)	- Solvents - Food ingredients, flavors - Plastics and elastic fibers - Paints and coatings - Lubricating oils, engine coolants and deicers - Diesel fuel oxygenates - Personal care products and cosmetics - Detergents, air fresheners and household cleaners - Automotive and industrial cleaners - Paint strippers and graffiti removers - Chemical intermediate for herbicides, insecticides, and fungicides	- Agro Industrie Recherches et Développments (ARD), France - DNP Green Technology - Bioamber (JV: DNP and ARD) - US Department of Energy - National Research Council of Canada - Biotechnology Research Institute - Rice University - Roquette and DSM - University of Georgia - Toyota Tsusho Company, Japan (shareholder of Bioamber) - Michigan State University, Michigan - Biotechnology Institute - BioEnergy International (Myriant Technologies) - Mitsubishi Chemical Corporation - Luleå University of Technology, Sweden	Current petrochemical production processes for succinic acid and its derivatives are not cost competitive with other petrochemical derived materials, and thus, succinic acid is currently a high cost chemical that serves only in niche market applications. However, biobased production routes are currently being developed by numerous companies and research institutions, and if a cost competitive biobased production route for succinic acid were developed, succinic acid could potentially serve as a replacement or partial replacement for many petrochemicals currently on the market. In addition to the many market applications for which succinic acid and its derivative chemicals can be applied, another promising attribute is that its production requires CO <sub>2</sub> .	



Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>Fumaric Acid</b>	- Unsaturated succinate derivatives - Aspartic acid	<ul style="list-style-type: none"> <li>- Food acidulant</li> <li>- Polyester resins</li> <li>- Sweetener</li> <li>- Fabric dye</li> <li>- Animal feed</li> <li>- Alkyd resins - widely used in adhesives and paint</li> <li>- Printing Inks</li> <li>- Paper sizing</li> <li>- Cleaning agent</li> <li>- Food and beverage</li> <li>- Soaps, mouthwashes, and toothpaste</li> <li>- Throat lozenges, cough syrups, and effervescent powdered preparations</li> <li>- Skin care products</li> <li>- Animal feed</li> </ul>	- Delft University of Technology, Netherlands	Base technology is commercialized, but research efforts on efficient, low cost production methods for fumaric acid and its derivatives via fermentation are ongoing.	
<b>Malic Acid</b>	- Hydroxy succinate derivatives	<ul style="list-style-type: none"> <li>- Potential replacement for terephthalic acid, a widely used component in various polyesters, such as polyethylene terephthalate (PET) and polybutyleneterephthalate (PBT)</li> <li>- New polyesters and nylons</li> <li>- Adhesives, coatings, inks, composites, binders, and/or foams</li> <li>- Pharmaceuticals</li> <li>- Agrochemicals</li> <li>- Antibacterial agents</li> <li>- Fragrances</li> <li>- (see above uses of succinic acid)</li> </ul>	- Delft University of Technology, Netherlands	Base technology is commercialized, but research efforts on efficient, low cost production methods for malic acid and its derivatives via fermentation are ongoing.	
<b>2,5-Furan Dicarboxylic Acid (FDCA)</b>	<ul style="list-style-type: none"> <li>- 2,5-Dihydroxymethylfuran</li> <li>- 2,5-Bis(hydroxymethyl) tetrahydrofuran</li> <li>- 2,5-Bis(aminomethyl) tetrahydrofuran</li> <li>- 2,5-Furandicarbaldehyde</li> <li>- Succinic Acid</li> </ul>	<ul style="list-style-type: none"> <li>- Potential replacement for terephthalic acid, a widely used component in various polyesters, such as polyethylene terephthalate (PET) and polybutyleneterephthalate (PBT)</li> <li>- New polyesters and nylons</li> <li>- Adhesives, coatings, inks, composites, binders, and/or foams</li> <li>- Pharmaceuticals</li> <li>- Agrochemicals</li> <li>- Antibacterial agents</li> <li>- Fragrances</li> <li>- (see above uses of succinic acid)</li> </ul>	<ul style="list-style-type: none"> <li>- Canon</li> <li>- Batelle, Memorial Institute</li> <li>- Technical University of Denmark</li> <li>- Danish National Advanced Technology Foundation</li> <li>- Institute of Technology, Federal Agricultural Research Centre, Germany</li> </ul>	Base technology is still under investigation.	



Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>3-Hydroxy-propionic Acid (3-HPA)</b>	<ul style="list-style-type: none"> <li>- 1,3-Propanediol</li> <li>- Acrylic Acid</li> <li>- Methyl Acrylate</li> <li>- Acrylamide</li> <li>- Malonic Acid</li> <li>- Ethyl 3-HP</li> <li>- Propiolactone</li> <li>- Acrylonitrile</li> </ul>	<ul style="list-style-type: none"> <li>- Solvents</li> <li>- Plastics and moldings</li> <li>- Fibers and resins</li> <li>- Composites</li> <li>- Adhesives</li> <li>- Laminates, floor polishes, paints and coatings</li> <li>- Aliphatic polyesters and copolyesters</li> <li>- Wastewater treatment</li> <li>- Gel electrophoresis</li> <li>- Papermaking</li> <li>- Ore processing</li> <li>- Permanent press fabrics.</li> <li>- Vitamins</li> <li>- Disinfectant; has been used to sterilize blood plasma, vaccines, tissue grafts, surgical instruments, and enzymes.</li> </ul>	<ul style="list-style-type: none"> <li>- Cargill</li> <li>- Codexis</li> <li>- Pacific Northwest National Laboratory</li> <li>- Novozymes</li> <li>- DOE</li> <li>- Qingdao Institute of Biomass Energy and Bioprocess Technology (China)</li> <li>- Perstorp (Sewden)</li> </ul>	<p>There is currently no commercially viable production route for 3-HPA using petrochemical feedstocks. Yet, many of the derivative chemicals that can be produced from 3-HPA are commercially produced from fossil fuel feedstocks. Cargill, along with Codexis and the Pacific Northwest National Laboratory, have developed a bioprocess to produce 3-HPA. In this process glucose or another carbohydrate source is converted into 3-HPA using a multi-step enzymatic reaction within the cells of a microorganism. 3-HPA can then be converted into a variety of high-value chemicals. In early 2008, Cargill announced a joint agreement with Novozymes to develop technology enabling the production of acrylic acid via 3-HPA. At the time of the announcement, the companies said that they expected the technology to be ready in 5 years.</p>	



Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>Aspartic Acid</b>	<ul style="list-style-type: none"> <li>- Amine Tetrahydrofuran</li> <li>- Amine Butyrolactone</li> <li>- Amine Butanediol</li> <li>- Aspartic Anhydride</li> <li>- Polyaspartic acid and Polyasparates</li> <li>- Amino-2-Pyrrolidone</li> </ul>	<ul style="list-style-type: none"> <li>- Salts for chelating agent</li> <li>- Sweeteners</li> <li>- Pharmaceuticals</li> <li>- Polyaspartic acid, synthetic resins, and cosmetics</li> <li>- Potential for polymer and solvent applications</li> <li>- Novel polyester - potential exists as a drug delivery biomaterial.</li> <li>- Novel polymers that could be substituted for polyacrylic acid and polycarboxylates. Potential applications include: a suspending and textile-sizing agent, adhesives, paints, hydraulic fluids, detergents, water treatment systems, corrosion inhibition, and super-absorbents.</li> </ul>	- Massachusetts Institute of Technology	Can be produced directly from sugar substrate or from fumaric acid and ammonia feedstocks. Currently, aspartic acid is commercially produced from fumaric acid for some high value market applications; therefore, reducing the cost of fumaric acid production would decrease the cost of aspartic acid, making it more competitive across a wider range of product applications. However, if the technical performance of producing aspartic acid directly from the sugar substrate could be improved, this route could be cheaper. A direct fermentation from sugar route is not yet economical.	
<b>Glucaric Acid</b>	<ul style="list-style-type: none"> <li>- Glucaroyl-Lactone</li> <li>- Glucaroyl-δ-Lactone</li> <li>- Glucarodilactone</li> <li>- Polyhydroxy-polyamides</li> <li>- α-Ketoglucarates</li> <li>- Esters and Salts</li> </ul>	<ul style="list-style-type: none"> <li>- Solvents</li> <li>- Nylons</li> <li>- Detergent surfactant</li> <li>- Dietary supplements (some evidence suggests that glucaric acid may reduce the risk of cancer development - not strongly supported).</li> <li>- Other potential uses range from human therapeutics to polymer synthesis.</li> </ul>	- Massachusetts Institute of Technology	Two different pathways for the synthesis of glucaric acid from glucose are currently being researched by the Massachusetts Institute of Technology.	





Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>Glutamic Acid</b>	<ul style="list-style-type: none"> <li>- Glutaminol</li> <li>- Norvaline</li> <li>- 5-Amino-1-Butanol</li> <li>- 1,5-Pentandiol</li> <li>- Glutaric Acid</li> <li>- Pyroglutaminol</li> <li>- Proline</li> <li>- Prolinol</li> <li>- Pyroglutamic Acid</li> </ul>	<ul style="list-style-type: none"> <li>- Food flavoring agent</li> <li>- Pharmaceuticals</li> <li>- Surfactants</li> <li>- Fabric coatings</li> <li>- Moisturizer in cosmetics</li> <li>- Production of polymers such as polyester polyols and polyamides.</li> <li>- Potential uses similar to BDO, THF, GBL</li> </ul>	<ul style="list-style-type: none"> <li>- Pacific Northwest National Laboratory</li> <li>- Cerestar Holding B.V., Netherlands</li> <li>- University of Minnesota</li> <li>- Tufts University School of Medicine</li> </ul>	Base technology is commercialized, but research efforts on efficient, low cost production methods for the production of glutamic acid and its derivatives are ongoing.	
<b>Itaconic Acid</b>	<ul style="list-style-type: none"> <li>- 3- &amp; 4- Methyl-GBL</li> <li>- 3-Methyl THF</li> <li>- 2-Methyl-1,4-BDO</li> <li>- 3- &amp; 4- Methyl-NMP</li> <li>- 2-Methyl-1,4-Butanediamine</li> <li>- 3-Methylpyrrolidine</li> <li>- Itaconic Diamide</li> </ul>	<ul style="list-style-type: none"> <li>- New properties for the BDO, GBL, and THF family of polymers.</li> <li>- Acrylic fibers and rubbers, reinforced glass fiber, artificial diamonds and lens.</li> <li>- Paints, coatings, adhesives, thickeners, and binders</li> <li>- Water treatment systems</li> <li>- Detergent</li> <li>- Lubricant oil</li> <li>- Carpets</li> <li>- Pharmaceuticals</li> <li>- Potential as a component of P-series fuels<sup>a</sup></li> </ul>	<ul style="list-style-type: none"> <li>- TNO Quality of Life, Netherlands</li> <li>- National Science Council, Taiwan</li> <li>- USDA, ARS</li> </ul>	Base technology is commercialized, but research efforts on efficient, low cost production methods for the production of itaconic acid and its derivatives are ongoing.	








Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>Levulinic Acid</b>	<ul style="list-style-type: none"> <li>- 2-Methyl-THF</li> <li>- g-Valerolactone</li> <li>- Angelilactones</li> <li>- 1,4-Pentanediol</li> <li>- b-Acetylacrylic Acid</li> <li>- Diphenolic Acid</li> <li>- Levulinic Esters</li> <li>- d-Aminolevulinic</li> <li>- Acrylic Acid</li> </ul>	<ul style="list-style-type: none"> <li>- Food/beverage acidulant</li> <li>- Nylon, synthetic rubbers and plastics</li> <li>- Pharmaceuticals</li> <li>- Cigarettes</li> <li>- Potential as a component of P-series fuels</li> <li>- Solvent</li> <li>- Coatings</li> <li>- Perfume and flavor industries</li> <li>- Pesticides and herbicides</li> <li>- Copolymerization with other monomers for property enhancement</li> <li>- Polycarbonate synthesis</li> </ul>	<ul style="list-style-type: none"> <li>- Maine BioProducts (Biofine)</li> <li>- BioMetrics, Inc</li> <li>- Pacific Northwest National Laboratory and NREL</li> </ul>	<p>Maine BioProducts' Biofine process is a thermochemical process using acid hydrolysis to produce levulinic acid and other co-products (e.g., furfural, formic acid, and char) from cellulose. In addition to being a building block chemical for many other high-value chemicals, levulinic esters (85%) mixed with other alcohols (e.g., ethanol, methanol, butanol) produce a desirable fuel product; clean burning (burns cleaner than pure hydrocarbon products), can be transported via pipeline, low cloud point in diesel blends (lower than biodiesel), higher mpg than ethanol, soot reduction, and exceeds ASTM D-975 standards. For this reason, the strategy of Maine BioProducts is to co-locate their Biofine process along with existing/future bio-alcohol (e.g. ethanol, cellulosic ethanol, butanol) supplies.</p> <p>Processes are still being developed to produce derivatives from levulinic acid; some of these processes are further along than others.</p>	
<b>3-Hydroxy-butyrolactone</b>	<ul style="list-style-type: none"> <li>- 3-Hydroxy-tetrahydrofuran</li> <li>- 3-Amino-tetrahydrofuran</li> <li>- 2-Amino-3-Hydroxy-tetrahydrofuran</li> <li>- Acrylate-Lactone</li> <li>- Epoxy-Lactone</li> <li>- g-Butenyl-Lactone</li> </ul>	<ul style="list-style-type: none"> <li>- High value pharmaceutical applications</li> <li>- Solvents</li> <li>- Lycra fibers</li> </ul>	<ul style="list-style-type: none"> <li>- Michigan State University</li> </ul>	<p>While there are research efforts looking at developing efficient, low cost production methods for 3-hydroxybutyrolactone and its derivatives, there is relatively little incentive to develop this specialty chemical with high-value use into a commodity chemical.</p>	

Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>Glycerol (glycerin)</b>	<ul style="list-style-type: none"> <li>- Glyceric Acid</li> <li>- 1,3-Propanediol (PDO)</li> <li>- Propylene Glycol (PG)</li> <li>- Branched polyesters and nylons</li> <li>- Glycidol</li> <li>- Propanol</li> <li>- Mono-, Di-, or Tri-Glycerate</li> <li>- Diglyceraldehyde</li> <li>- Glycerol Carbonate</li> </ul>	<ul style="list-style-type: none"> <li>- Cosmetic and personal/oral care products</li> <li>- Pharmaceuticals</li> <li>- Foods/beverages</li> <li>- Fuels</li> <li>- Polyether polyols (for polyurethane) and for polyol foams</li> <li>- Polyactic acid with better polymeric properties and polyester fibers with new properties</li> <li>- Adhesives, laminates, coatings, and moldings</li> <li>- Aliphatic polyesters and copolyesters.</li> <li>- Solvent</li> <li>- Antifreeze</li> <li>- Unsaturated polyurethane resins for use in insulation</li> </ul>	<ul style="list-style-type: none"> <li>- Current biodiesel manufacturers</li> <li>- University of Wisconsin (tech Glycerol to PG)</li> </ul> <p>Developing Fuel Applications:</p> <ul style="list-style-type: none"> <li>- Diversified Energy Corporation</li> <li>- North Carolina State University</li> <li>- XcelPlus Global Holdings Inc.</li> <li>- Institut Universitari de Ciència i Tecnologia (Barcelona, Spain)</li> <li>- Virent Energy Systems Inc.</li> <li>- New Century Lubricants</li> <li>- Rice University / Glycol</li> </ul> <p>Biotechnologies</p>	<p>While glycerol can be produced from the sugars present in corn and corn biomass, current production of glycerol largely comes as a by-product of biodiesel production.</p> <p>There are several routes to produce PG using glycerin. Generally, glycerin is hydrogenated in the presence of metallic catalysts and hydrogen under different reaction conditions. Additionally, microbial conversion of glycerol to PG has also been evaluated.</p> <p>There are numerous companies currently developing technologies to produce fuel products from glycerol.</p>	
	<b>Sorbitol / Isosorbide</b>	<ul style="list-style-type: none"> <li>- Food; sugar substitute</li> <li>- Laxative</li> <li>- Pharmaceuticals</li> <li>- Cosmetics and personal care products</li> <li>- Adhesives</li> <li>- Paper products</li> <li>- Textiles</li> </ul>	<ul style="list-style-type: none"> <li>- Roquette</li> <li>- Archer Daniels Midland</li> <li>- Danisco</li> <li>- SPI Polyols</li> <li>- Cargill</li> <li>- BASF</li> <li>- Bayer AG</li> <li>- Pacific Northwest National Laboratory (PNNL)</li> </ul>	<p>Production of sorbitol is well developed; however, low cost technologies for the production of its derivatives, such as isosorbide, are currently being developed (see below). Additionally, Pacific Northwest National Laboratory is also trying to develop a more environmentally benign sorbitol production process that would not use mineral acid catalysis, which creates separation and waste disposal issues.</p>	



Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>Isosorbide</b>	<u>Derived from:</u> - Sorbitol <u>Derivatives:</u> - Isosorbide Diglycidyl Ether Resins - Dimethyl Isosorbide - Mono and Dinitrate Isosorbide - Isosorbide Diesters	- Increases the strength and rigidity, particularly under high temperatures, of polymers such as polyethylene terephthalate (PET), which are used widely to manufacture food and beverage containers. - Potential as a liner in food and beverage cans - CDs - Pharmaceuticals and fine chemical market - High performance fibers - Solvent - Skin-care products	- Roquette - Iowa Corn Promotion Board - Pacific Northwest National Laboratory - General Electric Global Research - New Jersey Institute of Technology - Monsanto EnviroChem	Various processes are actively being developed by a range of companies to economically produce isosorbide from commercially available sorbitol.	
<b>Propylene Glycol (PG)</b>	<u>Derived from:</u> - Lactic acid - Glycerin - Sorbitol	- Surface coatings - Glass fiber resins - Antifreeze - Solvents - Humectant - Manufacturing of plasticizers - Hydraulic brake fluids - Non-ionic detergents - Emulsifier - Heat transfer fluid - Moisturizer - Unsaturated polyester resins (e.g., boat hull)	- Pacific Northwest National Laboratory (PNNL) - Archer Daniels Midland - Cargill / Ashland Chemical - Davy Process Technology - Dow Chemical - Huntsman Corporation - Michigan State University - Senenergy Chemical - University of Wisconsin	PNNL is working to develop a cost efficient production process to produce PG from sorbitol. There are also several routes to produce PG using glycerin. Generally, glycerin is hydrogenated in the presence of metallic catalysts and hydrogen under different reaction conditions. Microbial conversion of glycerol to PG has also been evaluated.	



Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>Xylitol/ Arabinitol</b>	<ul style="list-style-type: none"> <li>- Xylaric Acid</li> <li>- Propylene Glycol</li> <li>- Ethylene Glycol</li> <li>- Lactic Acid</li> <li>- Glycerol</li> <li>- Mixture of Hydroxyfurans</li> </ul>	<ul style="list-style-type: none"> <li>- Foods</li> <li>- Oral hygiene products (mouthwash and toothpaste)</li> <li>- Pharmaceuticals</li> <li>- Dietetic products</li> <li>- Cosmetics</li> </ul>	<ul style="list-style-type: none"> <li>- Virginia Polytechnic Institute</li> <li>- DNP International</li> <li>- Federal University of Viçosa, Brazil</li> <li>- ARS</li> <li>- ZuChem</li> <li>- DFI (licensed tech from Purdue University)</li> </ul>	<p>Xylitol is currently commercially available; however, commercial-scale quantities are typically derived from birch-wood fibers that have been subjected to a combination of acids, high pressures and temperatures, chemical catalysts, and a series of separation and purification steps. Cost efficient production routes via corn fiber are being developed and improved. DFI has licensed a potentially breakthrough process for the production of xylitol from Purdue University.</p>	
<b>Methyl Ethyl Ketone (MEK)</b>		<ul style="list-style-type: none"> <li>- Solvents</li> <li>- Paints and coatings</li> </ul>	<ul style="list-style-type: none"> <li>- Genomatica</li> </ul>	<p>Genomatica has developed a process to produce MEK using existing ethanol manufacturing infrastructure. The process uses the same equipment, temperatures, and processes. The development comes in the form of a new organism that converts sugar and water into MEK.</p>	
<b>Furfural</b>		<ul style="list-style-type: none"> <li>- Fuel</li> <li>- Solvents</li> </ul>	<ul style="list-style-type: none"> <li>- Raven Biofuels</li> <li>- Lignol Innovations Ltd.</li> <li>- Avantium</li> <li>- University of California, Davis</li> </ul>	<p>- Steam Distillation: The 6-carbon sugars are processed into ethanol through a normal fermentation process and the 5-carbon sugars are removed and processed via steam distillation of the acidified hemicellulose into furfural.</p> <p>- Catalytic</p> <p>- Non-Fermentative: A production process whereby furfural is produced without fermentation, enzymes, or pretreatments, using hydrochloric acid.</p>	
<b>Hydroxy-methylfurfural (HMF)</b>		<ul style="list-style-type: none"> <li>- Fuel</li> <li>- Plastics</li> </ul>	<ul style="list-style-type: none"> <li>- Pacific Northwest National Laboratory</li> </ul>	<p>Researchers believe they have discovered a one step process to convert cellulose into HMF. Recyclable catalysts are used in tandem to break down the cellulose into glucose and then convert the glucose into HMF.</p>	


Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>Methyl Halides</b>		<ul style="list-style-type: none"> <li>- Solvents</li> <li>- Propellants</li> <li>- Soil fumigants</li> <li>- Fuel</li> <li>- Aromatics</li> </ul>	<ul style="list-style-type: none"> <li>- University of California - San Francisco</li> </ul>	An engineered bacterial/yeast duo have successfully converted sugarcane bagasse, corn stover, switchgrass and poplar into methyl halide, a chemical that is commonly used in the petrochemical industry. Using zeolite catalysts, the methyl halides can be manufactured into gasoline, olefins, aromatics, alcohols, ether, and other chemicals.	
<b>1,4-Butanediol (BDO)</b>	<ul style="list-style-type: none"> <li>- Polybutylene succinate (PBS)</li> <li>- Polybutylene succinate adipate (PBSA)</li> <li>- Polybutylene succinate terephthalate</li> <li>- Polybutylene terephthalate (PBT)</li> <li>- Thermoplastic polyurethanes</li> <li>- Tetrahydrofuran (THF)</li> <li>- γ-Butyrolactone (GBL)</li> <li>- Polytetramethylene Glycol (PTMG)</li> </ul>	<ul style="list-style-type: none"> <li>- Solvents</li> <li>- Plastics and packaging</li> <li>- Paints and coatings</li> <li>- Elastic fibers</li> <li>- Hair and scalp conditioners</li> <li>- Automotive applications: hoses, belts, gaskets, grease boots, CV joints, wire and cable insulations, spacers, and bushings</li> <li>- Many polyurethane and polyester applications</li> </ul>	<ul style="list-style-type: none"> <li>- Genomatica</li> <li>- BioAmber</li> </ul>	<p>BDO is most commonly produced via petrochemical feedstocks. In September of 2008, Genomatica announced its novel technology development to produce BDO directly from sugars, and has since continued to make improvements designed to make the process more cost effective and productive.</p> <p>Other companies developing biobased succinic acid are also working on cost efficient production of BDO via succinic acid.</p>	

Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>1,3-Propanediol (PDO)</b>	- Polytrimethylene Terephthalate (PTT) - Polyurethane and polyesters	- Polymer with remarkable "stretch-recovery" properties - Textiles - clothing and upholstery - Adhesives - Antifreeze and lubricants - Pharmaceuticals - Fragrances - Fabric softener - Vitamin H - Composites - Moldings - Paints and coatings  New Use: Scratch-resistant varnish	- DuPont Tate & Lyle BioProducts (Sorona) - Genencor International - Pacific Northwest National Laboratory - DOE	PDO was historically produced via petrochemical based feedstocks. More recently, biobased production routes have been developed. The bioprocessing of (PDO) developed by DuPont and Genencor is claimed to be economically competitive with petrochemical production routes.	
<b>Polyhydroxyalkanoates (PHAs)</b>	- Poly-beta-hydroxybutyrate - PHB - Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) - PHBV	- Thermoplastic or elastomeric plastics - Packaging - Pharmaceuticals - Medical devices and tissue engineering	- Hawaii Natural Energy Institute and the University of Hawaii - I-PHA BioPolymers, Hong Kong (licensed University of Hawaii technology) - Metabolix - Monsanto (Biopol) - DOE - Biomer, Germany - Proctor & Gamble - Mitsubishi Gas, Japan - PHB Industrial, Brazil - Tianan Biologic Material Co, Ltd Ningbo, China - Bio-on	In June 2005, Metabolix received the US Presidential Green Chemistry Challenge Award (small business category) for their development and commercialization of a cost-effective method for manufacturing PHAs.  While already commercially produced, a process is being developed to produce this class of bioplastics as a by-product of cellulosic ethanol production, a process that would reduce greenhouse gas emissions.	
<b>Lysine</b>	- Caprolactam	- Animal feed - Pharmaceutical  New Use: "AlsoSalt" - a no sodium salt substitute	- ADM - Ajinomoto - CJ Corp - Degussa - BASF	New technology developments, such as the production of caprolactam from lysine could increase future market demand for lysine (see below).	



Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>Caprolactam</b>	- Polyamide-6 (Nylon-6) <u>Derived from:</u> -Lysine	- Fibers and textiles - Tires - Engineering plastics in structural material for applications in the automotive and electronics industries - Packaging - Film coating - Plasticizers and polyurethanes - Paint	- Michigan State University	New technologies are being developed to produce caprolactam from lysine.	
<b>Lactic Acid</b>	- Polylactic acid - Ethyl Lactate - Acrylic Acid - Propylene Glycol - Pyruvic Acid - 1-Amino-2-Propanol - Lactonitrile - Lactic Amide - Lactide - 2,5-Dimethyl-1,4-Dioxane	- Food/Beverage - acidulant - Electroplating bath additive - Mordant - Film and thermoformed packaging - Consumer electronics - Textiles - clothing, upholstery, and carpet - Personal care products - Solvents - Detergents - Super absorbent polymers - diapers - Coatings - Antifreeze, hydraulic brake fluids - Cleaning product	- Cargill (NatureWorks) - PURAC - NREL - Institute of Chemical Technology Prague	Research efforts have been directed toward developing ways to improve the yields of lactic acid via the fermenting microorganism Lactobacillus and various fungal strains, and to produce lactic acid using lignocellulosic feedstocks.  Also, the production of polylactic acid via lactic acid has been recently commercialized and the process has been improved since its initial commercialization (see polylactic acid).	

Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>Polylactic Acid (PLA)</b>	Derived from: - Lactic acid	- Film and thermoformed packaging - Textiles - clothing, upholstery, carpet, and diapers - Personal care products	- Cargill (NatureWorks) - PURAC	Technology whereby polylactic acid is converted from lactic acid, a fermentation product of biomass sugars. This commercially produced product is cost competitive with conventional polymers and has many performance properties equal to or greater than conventional polymers such as polyethylene terephthalate (PET) and nylon. The company has made improvements to its process since its commercial debut that have further reduced CO <sub>2</sub> emissions and reduced process energy requirements. Additionally, the company is looking to develop fermentation organisms to convert 5-carbon sugars as well as glucose into PLA.	 e
<b>Acrylic Acid</b>	Derived from: - Lactic Acid - 3-Hydroxypropionic Acid	- Coatings and adhesives - Super absorbent polymers (e.g. diapers) - Detergents - Plastics - Fibers	- Cargill - Novozymes	Acrylic acid is most commonly produced via petrochemical feedstocks (e.g. propylene). Commercially viable biobased production route is yet to be established. In early 2008, Cargill announced a joint agreement with Novozymes to develop technology enabling the production of acrylic acid via 3-HP. At the time of the announcement, the companies said that they expected the technology to be ready in 5 years.	

Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>2</sup>	Description of Technology	Stage of Development
<b>Ethyl Lactate</b>	Derived from: - Lactic acid	- Solvents - Pharmaceuticals - Food - Fragrances	- DOE - Vertec Biosolvents Inc. - Argonne National Laboratory - Cargill - Ashland Specialty Chemical Company - University of Pennsylvania - Michigan State University	Although ethyl lactate has been around for years, the cost of producing it has been too high to allow it to compete economically with lower-priced chemical solvents. Advancements in lactic acid separation technologies using electro dialysis, advanced membrane, and reactive separations have decreased ethyl lactate costs, making it more competitive with other commercially available solvents. Argonne Laboratory has developed a process based on a selective membrane separation and purification process that permits low-cost synthesis of high-purity ethyl lactate from fermentation-derived lactic acid. The University of Pennsylvania has been developing an integrated semi-continuous distillation, reaction, and pervaporation process for the production of ethyl lactate from ethanol and lactic acid. Michigan State University researchers have demonstrated the effectiveness of applying their reactive distillation technology to the production of ethyl lactate from lactic acid and ethanol.	

\* Red = DOE Top 12 Value-Added Chemicals from Sugars and Syngas

1/ Not an exhaustive list

2/ Not an exhaustive list. Some companies/institutions may no longer be involved, some may be working with one another, and some may only be financially involved.

a/ According to the DOE a "P-Series fuel is a blend of natural gas liquids (pentanes plus), ethanol, and the biomass-derived co-solvent methyltetrahydrofuran (MeTHF). P-Series fuels are clear, colorless, 89-93 octane, liquid blends that are formulated to be used in flexible fuel vehicles (FFVs)."







b/ Sorbitol is already commercially produced. However, technology developments to lower production costs and to produce derivatives such as isosorbide could expand this product's market demand.

c/ The production of PG via some technologies and base chemicals is already commercialized (e.g., traditional hydrogenation of glycerol), while production via other technologies and base chemicals (e.g., from sorbitol) are still being developed. Many of the companies listed are focusing on PG from glycerin, the by-product of biodiesel production.

d/ While already commercialized, other processes are still being developed.





e/ In a March 09 article, Cargill announced it was looking at prospective locations for a second plant. The company "anticipates continued advancements in the resin's performance, as well as an increase in the number of products and applications using Ingeo."







Table 27: New Uses of Corn Cobs

Biobased Products/Chemicals <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>1</sup>	Description of Technology (if applicable)	Stage of Development
Anhydrous Ammonia	- Fuel - Fertilizer	- SynGest Inc.	SynGest Inc. is employing a gasification process which uses corn biomass, initially corn cobs, to produce anhydrous ammonia for fuel and fertilizer. The company plans to originally produce fertilizer, but in the long run, intends to produce fuel as well. The company claims to have a carbon negative process and low production costs that can undercut the cost of ammonia produced from natural gas.	
Energy (natural gas substitute)	- Energy	- Chippewa Valley Ethanol Company - Frontline BioEnergy Gasifiers - University of Minnesota	Chippewa Valley Ethanol Company (CVEC) plans to use corn cobs and other biomass to run its ethanol plant using Frontline BioEnergy's biomass gasification technology. CVEC's plant engineer says that the "cobs could cut the plant's energy cost by one fourth or more."	
Cellulosic Ethanol	- Fuel	- POET	Poet plans to begin producing 25 million gallons of cellulosic ethanol from corn cobs as early as 2011 at its Emmetsburg, IA biorefinery.	
Polishing Materials	- Polishing materials	- Andersons Inc.	N/A	
Animal Bedding	- Animal bedding	- Andersons Inc.	N/A	
Cat Litter	- Cat Litter	- Andersons Inc.	N/A	

1/ Not an exhaustive list

Table 28: New Uses of Distillers Grains




Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>1</sup>	Description of Technology (if applicable)	Stage of Development
<b>DDGS - Fillers in Plastics</b>	- DDGS fillers in plastics	- Adhesives - Furniture - Architectural panels - Composite molding applications - Golf tees	- University of Minnesota - USDA, ARS - South Dakota State University - Northern Illinois University (NIU)	N/A	
<b>DDGS - Zein</b>	- Corn Protein	- Biodegradable plastics - Food and paper coatings - Chewing gum base - Biodegradable textile fiber - Medical applications - Printing ink - Antioxidants - Adhesives and binders	- USDA, ARS	Currently, unpurified zein is used in specialty coatings. However, a new, cost-effective process to purify the zein makes the protein suitable for cosmetic, food, and biomedical applications.	
<b>DDGS - Fuel</b>	- Corn Fiber	- Fuel (ethanol or butanol)	- University of Illinois  - NREL - NCGA - Corn Refiners Association	The fiber portion of the DDGS is separated via the elusieve process. Then, after enzymatic hydrolysis the sugars can be fermented to produce butanol or ethanol.  NREL is working on designing unique biocatalysts to ferment arabinose, a major component in the available sugars from corn fiber, a residue of the corn-to-ethanol process, into ethanol.	
<b>DDGS - Energy</b>	- DDGS	- Energy	- Washington University - University of Minnesota - USDA, ARS - Iowa State University - Rein & Associates (MN) - Biogasol - POET - University of Borås - Kwartha Ethanol	-Anaerobic Digestion: Anaerobic digestion uses bacteria to convert the thin or whole stillage by-product of ethanol production into biogas, which can then be used to reduce natural gas usage. This process reduces energy costs and greenhouse gas emissions and helps to conserve water. - Direct Burning - Gasification	




Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>1</sup>	Description of Technology (if applicable)	Stage of Development
<b>DDGS - Fertilizer</b>	- DDGS	- Organic fertilizer	- USDA, ARS - Summit Seed Inc.	Researchers are now looking at the effectiveness of this application when the fiber and germ portion of the DDGS are removed prior to fermentation.	
<b>DDGS - Weed Control</b>	- DDGS	- Weed control	- USDA, ARS - Summit Seed Inc.	Researchers are now looking at the effectiveness of this application when the fiber and germ portion of the DDGS are removed prior to fermentation.	
<b>Corn Fiber Gum</b>	- Corn Fiber	- Emulsifier - flavor stabilizer in soft drinks - a substitute to the costly "gum arabic" that is currently imported from African countries.	- USDA, ARS - University of Illinois - University of Missouri	ARS researchers are using their elusive fractionation process to recover the fiber from the distillers grains at the back-end of the ethanol production process or fiber extracted from the corn wet milling process.	
<b>Astaxanthin</b>	- Corn Fiber	- High value specialty product used in the diets of farm-raised fish in order to give the flesh of salmonids, shrimps, lobsters, and crayfish the pinkish-red hue.	- USDA, ARS - Clemson University	Astaxanthin would be produced from the fermentation of corn fiber. Several strains of fermenting yeast are currently being explored.	
<b>DDGS - Flour</b>	- DDGS Flour	- Cookies, breads, pastas (While DDGS flour is nutritious, the fermentation process used to make ethanol tends to give the food product a bitter off-flavor and odor that lacks consumer appeal.)	- USDA, ARS - South Dakota State University	N/A	
<b>DDGS - Food Flavorant</b>	- DDGS	- Food flavorant - sodium flavor replacement	- Kraft Foods Holdings, Inc.	Patented application - Rather than using DDGS in food applications as a filler and trying to find ways to disguise its bitter taste, this application would use smaller amounts of DDGS and use its distinct flavor as a flavor substitute (e.g. sodium).	



1/ Not an exhaustive list



Table 29: New Uses of CO<sub>2</sub>



Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>1</sup>	Description of Technology (if applicable)	Stage of Development
CO <sub>2</sub> - Algae Production Systems	- Algae	- Biodiesel - Ethanol - Biocrude - renewable petroleum products: gasoline, diesel, and jet fuel	- Petrosun - Greenshift - Diversified Energy - Solazyme - Valcent - Green Star - Aurora Biofuels - XL Renewables - Others	The CO <sub>2</sub> emitted from the ethanol production process can be captured and used as a key input in the production of algae, which is in turn used to produce oil. Among other uses, this oil can then be used to make a range of fuel products.	
CO <sub>2</sub> - Biodegradable Plastics	- Biodegradable plastics	- Packaging - Insulating foam for buildings - Computer cases	- Novomer - Cornell University	This patented technology, which has been demonstrated on a small scale, mixes liquid metal with CO <sub>2</sub> or CO in a reactor at low pressure. Depending on the feedstock and the catalyst, the end product can be adjusted to be more flexible or slower to decompose.	
CO <sub>2</sub> - Oil Extraction	- Supercritical CO <sub>2</sub>	- Vegetable oil extraction from oilseeds - Potential also exists in algae oil extraction applications	- MOR Supercritical, LLC	Rather than using hexane, MOR Supercritical's technology uses carbon dioxide as their only solvent in their corn oil and oilseed extraction system. As opposed to conventional supercritical processes, MOR Supercritical claims that their technology greatly reduces operating costs which have prevented other supercritical systems from replacing petrochemical extraction using hexane, despite the numerous benefits. MOR Supercritical claims that their technology is energy efficient; automated, modular and scalable; has a small environmental footprint (1/6 of a typical solvent extraction plant); produces safe, solvent-free, non-degraded, high-quality products including undegraded meal with high protein digestibility; and an accompanying refining technology to extract and refine the oil in one step.	

Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>1</sup>	Description of Technology (if applicable)	Stage of Development
<b>CO<sub>2</sub> - Medical Implants - Drug Delivery</b>	- Supercritical CO <sub>2</sub>	- Used to push chemicals/medicines into a plastic that is often used in bone replacement	- Ohio State University	By using compressed CO <sub>2</sub> , researchers at Ohio State University discovered that they could alter the internal structure of plastic and create voids that could be used to hold medicine. The idea is that medicines implanted in bone replacements could help prevent inflammation and infection following surgery or serve as a means to dispense anti-tumor agents in patients where bone has been replaced as part of a cancer treatment program. Currently implants are sterilized with heat, radiation, and chemicals that can make embedded medicines less effective.	
<b>CO<sub>2</sub> - Sand and Magnesium Carbonate</b>	- Sand and Magnesium Carbonate	- Sand - Replacement for limestone in cement	- Pennsylvania State University - Los Alamos National Laboratory	Serpentine rock is mixed in a reactor with water and acid, in order to get magnesium and silica. Then, ammonia and CO <sub>2</sub> are added to get magnesium carbonate. Previous technologies which have attempted to store CO <sub>2</sub> in magnesium carbonate have been highly energy intensive due to high pressure requirements, while this proposed technology operates under ordinary pressures.  However, serpentine, which is plentiful near the Atlantic and Pacific coasts, is expensive to transport inland.	
<b>Carbon Sequestration</b>	-N/A	- CO <sub>2</sub> Storage	- Archer Daniels Midland	In an effort to decrease the carbon footprint of an ethanol facility, ADM is pursuing a project involving drilling an injection well 7,200 feet deep to store a total of 1 million metric tons of CO <sub>2</sub> .	

Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>1</sup>	Description of Technology (if applicable)	Stage of Development
<b>CO<sub>2</sub> - High Value Materials</b>	<ul style="list-style-type: none"> <li>- Formic Acid</li> <li>- Formate Salts</li> <li>- Oxalic Acid</li> <li>- Methanol</li> </ul>	<ul style="list-style-type: none"> <li>- A replacement for hydrochloric acid in the steel pickling process</li> <li>- Diesel fuel additive (ammonium formate)</li> <li>- Energy (hydrogen or methanol)</li> </ul>	<ul style="list-style-type: none"> <li>- Mantra Venture Group Ltd.</li> <li>- British Columbia's Clean Energy Research Center</li> </ul>	The Mantra Venture Group is working to develop a technology to convert CO <sub>2</sub> into formic acid and other high value materials by combining electricity with water, CO <sub>2</sub> and an electrolyte in a process they call electro-reduction.	
<b>CO<sub>2</sub> - Succinic Acid</b>	<ul style="list-style-type: none"> <li>- 1,4-Butanediol (BDO)</li> <li>- Tetrahydrofuran (THF)</li> <li>- γ-Butyrolactone (GBL)</li> <li>- 2-Pyrrolidinone</li> <li>- N-Methyl Pyrrolidone (NMP)</li> <li>- Polytetramethylene Glycol (PTMG)</li> <li>- Poly-Butylene Succinate (PBS)</li> <li>- Diethyl and Dimethyl Succinate (Succinic Acid + Ethanol/Methanol)</li> </ul>	<ul style="list-style-type: none"> <li>- Solvents</li> <li>- Food ingredients, flavors</li> <li>- Plastics and elastic fibers</li> <li>- Paints and coatings</li> <li>- Lubricating oils, engine coolants and deicers</li> <li>- Diesel fuel oxygenates</li> <li>- Personal care products and cosmetics</li> <li>- Detergents, air fresheners and household cleaners</li> <li>- Automotive and industrial cleaners</li> <li>- Paint strippers and graffiti removers</li> <li>- Chemical intermediate for herbicides, insecticides, and fungicides</li> </ul>	<ul style="list-style-type: none"> <li>- Agro Industrie Recherches et Développments (ARD), France</li> <li>- DNP Green Technology</li> <li>- Bioamber (JV: DNP and ARD)</li> <li>- US Department of Energy</li> <li>- National Research Council of Canada</li> <li>- Biotechnology Research Institute</li> <li>- Rice University</li> <li>- Roquette and DSM</li> <li>- University of Georgia</li> <li>- Toyota Tsusho Company, Japan</li> <li>- (shareholder of Bioamber)</li> <li>- Michigan State University, Michigan</li> <li>- Biotechnology Institute</li> <li>- BioEnergy International (Myriant Technologies)</li> <li>- Mitsubishi Chemical Corporation</li> <li>- Luleå University of Technology, Sweden</li> </ul>	CO <sub>2</sub> is used as input in the production process of succinic acid. Biobased production routes are currently being developed whereby succinic acid can be produced from a range of sugar feedstocks, including corn.	

1/ Not an exhaustive list

**Table 30: Lignin Derived Products**

Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>1</sup>	Description of Technology (if applicable)	Stage of Development
Power, Fuel, & Syngas	<ul style="list-style-type: none"> <li>- Ethanol</li> <li>- Process heat</li> <li>- Propanol</li> <li>- Butanol</li> <li>- Green fuels olefins</li> <li>- MeOH/DME</li> <li>- Fischer-Tropsch green fuels</li> <li>- Pyrolysis oil</li> <li>- Reformulated gasoline</li> </ul>	<ul style="list-style-type: none"> <li>- Fuel</li> <li>- Power</li> <li>- Solvents</li> <li>- Coatings - paint, varnish, and inks</li> <li>- Agricultural chemicals - insecticides, pesticides and herbicides</li> <li>- Synthetic resin and adhesives</li> <li>- Textiles (e.g., scatter rugs, bathmats)</li> <li>- Sealants</li> </ul>	N/A	Various technologies, including lignin combustion, gasification, pyrolysis, and hydroliquefaction can be used to produce these various products from lignin.	 a
Macro-molecules	<ul style="list-style-type: none"> <li>- Carbon fiber</li> <li>- Polymer fillers</li> <li>- Thermoset resins</li> <li>- Formaldehyde-free resins</li> <li>- Adhesives and Binders</li> </ul>	<ul style="list-style-type: none"> <li>- Steel panels in automobiles (reduces weight and improves fuel economy)</li> <li>- High strength engineering plastics</li> <li>- Heat-resistant polymers</li> <li>- Antibacterial surfaces</li> <li>- High strength and formaldehyde-free adhesives</li> <li>- Light and ultraviolet resistant polymers</li> <li>- Adhesives and binders</li> </ul>	N/A	Various technological developments have been made in this arena, and there are many more technical challenges still remaining to be solved.	







Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>1</sup>	Description of Technology (if applicable)	Stage of Development
Aromatics <sup>b</sup> - BTX (Benzene, Toluene, and Xylene) - Phenol - Terephthalic acid	- Benzene: Cyclo (hexane, hexanol, and hexanone), Caprolactam, Adipic Acid, 1,6-Diaminohexane, Cumene, and Styrene - Toluene: Dinitrotoluene, Diminotoluene, Toluene Diisocyanate, Benzoic Acid - Xylene: Isophthalic Acid and Terephthalic Acid - Phenol: Bisphenol A, Nitrophenols, Aminophenols, Cyclohexanone, and Cyclohexanol	- Pharmaceuticals - Synthetic rubbers - Upholstery - Car parts: body, bumpers, lighting, dashboard, seats, upholstery, fuel systems, under-the-bonnet components - Clothing - Plastics - CDs, CD-ROMs and DVDs	N/A	Various technological developments have been made in this arena, and there are many more technical challenges still remaining to be solved.	

1/ Not an exhaustive list

a/ Different technologies are at varying stages of development.






b/ According to the Pacific Northwest National Laboratory, "lignin is the only renewable source of an important and high-volume class of compounds - the aromatics."

**Table 31: Other New Corn Uses/Products**

Biobased Products/ Chemicals <sup>1</sup>	Derivatives/ Utilization <sup>1</sup>	Applications/End Uses <sup>1</sup> (Product and Derivatives)	Institutions/ Companies Involved <sup>1</sup>	Stage of Development
<b>AlsoSalt</b>	Produced from Lysine	- No sodium salt substitute (Product is being used in Heinz' no-salt added ketchup)	- Michigan State University - Diversified Natural Products, Inc.	
<b>Scratch-Resistant Varnish</b>	Produced from 1,3-Propanediol	- Scratch resistant furniture varnish	- Institute for Wood Research, Germany	
<b>HOLDOUT</b>	N/A	- A bio-based formulation to replace fluorinated compounds in paper-based food packaging products	- Cerealus - Maine Technology Institute	
<b>TerraMat (cork)</b>	N/A	- Corkboards - Floormats	- Purdue University	
<b>Melt-A-Way Cupcake Liners</b>	N/A	- Cupcake liner that is designed to become part of the cupcake during baking	- Purdue University	
<b>Nature's Silk</b>	N/A	- Biodegradable toilet paper	- Purdue University	

<sup>1/</sup> Not an exhaustive list

**Table 32: New Corn Varieties Designed for Food and Feed Applications**

Technology <sup>1</sup>	Description of Technology	Institutions/Companies Involved (Technology Name)	Stage of Development
<b>New Corn Varieties Designed for Food Applications</b>			
Food-Grade White and Yellow Corn Hybrids	These hybrids are targeted toward the wants and needs of food processors, designed for characteristics such as kernel density, composition, size, and ear rot disease.	- Pioneer	
High Extractable Starch and Waxy Corn	These hybrids have above average levels of extractable starch, a characteristic that is beneficial for wet milling.	- Pioneer	
Extrax Corn	Monsanto is in the fourth and final stage prior to product launch of their high oil corn (7% compared to 3.5%) for use in Renessen's (JV between Monsanto and Cargill) Extrax corn fractionation system. They are focusing on higher oil content as this is the most valuable fraction of the corn.	- Monsanto	
<b>New Corn Varieties Designed for Animal Feed Applications</b>			
High Available Energy	Hybrids with above average digestible energy for increased feeding value for pork and poultry producers.	- Pioneer	
Mavera™ High Value Corn with Lysine	Corn with higher levels of lysine, reducing need for lysine supplements in swine and poultry diets.	- Renessen LLC. (JV: Cargill and Monsanto)	

\*Some of these technologies can also be used to improve ethanol production economics and are dually listed above in Table 24.



## Appendix B: Traditional Corn-to-Ethanol Production Processes

There are two production processes for grain-based ethanol production – wet milling and dry milling. The main difference between the two is in the initial preparation of the grain prior to fermentation, and as a result the dry milling process is less capital intensive and production costs are lower. However, whereby the wet milling process results in multiple co-product streams (e.g., corn oil, corn gluten meal, corn gluten feed, and ethanol/chemicals, starch, or corn syrup), the dry milling process results in two products (e.g. ethanol and distillers grains). In the U.S., dry mill facilities account for the overwhelming majority of ethanol production capacity (85-90%).

### A. Traditional Dry Milling Ethanol Production Process

The process steps involved in traditional dry milling ethanol production are detailed below and illustrated within Figure 24.

In dry milling, the corn kernel is first removed from the husk and chaff. Then, the entire kernel is ground into a fine meal to expose the starch in what is often referred to as a hammer mill. Although processes vary, most dry mill facilities continue the process without separating out the various component parts of the kernel.

The meal is then sent to the “cooker” and mixed with water and amylase enzymes. Ammonia is also added for pH control and as a nutrient to the yeast (used in the next step of fermentation). Initially, the mixture is “jet cooked” for a brief period of time at 105-110°C. Then, the temperature is brought down to 70-95°C for about 1-2 hours. The heat is used to help rupture the cell walls and to reduce bacteria levels, as bacteria would otherwise compete with the yeast for the sugar feed. During this time, the amylase enzymes break down the exposed starch into dextrans (5 to 10 glucose molecule chains), which are water soluble. This water solubility is what causes the meal and water mixture to liquefy into what is referred to as a mash. For this reason, this particular process step is often referred to as “liquefaction”. After cooling the mash to 30-60°C and adjusting the pH, glucoamylase enzymes are added to further break down the dextrans into glucose molecules. This step is referred to as “saccharification”. The objective is to get the final solution to a point where the glucose or simple sugar concentration is between 20-24%.

The mash is then transferred to fermenters and mixed with yeast, typically of the genus *Saccharomyces*. The yeast then changes the sugar (glucose) into ethanol and carbon dioxide. It takes about 40-50 hours for the mash to ferment. During this time, the temperature, pH, and various nutrient concentrations must be controlled to maximize ethanol production. As the ethanol concentration of the

mixture increases, it becomes toxic to the yeast and the sugar fermentation process begins to slow down.

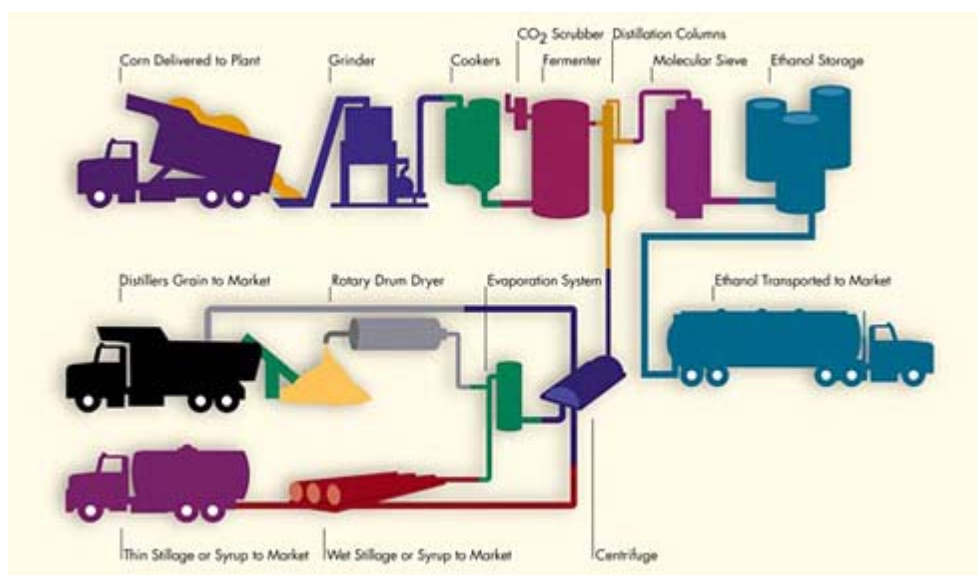
In the newer ethanol plants, the saccharification and the fermentation steps are often combined into one, referred to as Simultaneous Saccharification and Fermentation (SSF). In SSF, the glucoamylase enzymes and the yeast are added to the mash at the same time, allowing the yeast to metabolize the glucose at the same time it is produced. This limits the chances that undesired microbes/bacteria will consume the glucose before the yeast gets a chance.

The fermented mash, called “beer”, contains about 10-15% ethanol by volume. The rest of the mixture is water and grain/yeast solids that could not be fermented. To separate the ethanol, the mixture is sent to the distillation column and heated once again - this time to a temperature at which ethanol vaporizes, but the remaining materials do not. The ethanol vapor is collected and cooled, where it condenses to its liquid form. At this stage, the ethanol is concentrated to 190 proof (95% alcohol).

To purify the ethanol and remove any remaining water, it's passed through a dehydration system (e.g., molecular sieve), creating anhydrous ethanol. After this step, the ethanol is approximately 200 proof (100%). All water must be removed because a water-alcohol mixture cannot dissolve in gasoline. The anhydrous ethanol is then blended with 1% (2-5% in the U.S.) denaturant such as gasoline to make the ethanol unfit for human consumption - a requirement for fuel-grade ethanol. It is then ready for shipment to gasoline terminals or retailers.

Meanwhile, the remaining product at the bottom of the distillation column, known as the stillage is sent through a centrifuge that separates the water/solubles (~90%) from the non-fermentable solids (~10%). The solubles are then concentrated to about 30% solids by evaporation, resulting in Condensed Distillers Solubles (CDS) or “syrup.” The coarse grain or non-fermentable solids is then referred to as wet distillers grains (WDG) and can be marketed as such, or it can be mixed with the CDS and sold as wet distillers grains with solubles (WDGS). Alternatively the WDG can also be dried to form dried distillers grains (DDG) or mixed with CDS and dried to form dried distillers grains with solubles (DDGS). WDGS and DDGS are often used as a high protein feed source suitable for livestock. Generally, due to drying costs, distillers grains sold to nearby livestock operations, particularly dairy or beef cattle, are sold in the form of WDGS. However, swine, poultry and more distant beef or dairy operations typically receive DDGS.

Depending on local demand, the CO<sub>2</sub> produced during fermentation can either be released directly into the atmosphere or captured and sold for use in many food preparations and other industrial processes, such as carbonating beverages and the manufacture of dry ice.

**Figure 24: Traditional Dry Milling Ethanol Production Process**

Source: Renewable Fuels Association

## B. Traditional Wet Milling Ethanol Production Process

The process steps involved in traditional wet milling ethanol production are detailed below and illustrated within Figure 25.

In wet milling, the grain is soaked or "steeped" in water and dilute sulfurous acid for 24 to 48 hours. This steeping facilitates the separation of the grain into its many component parts such as starch, protein, germ and fiber in an aqueous medium prior to fermentation.

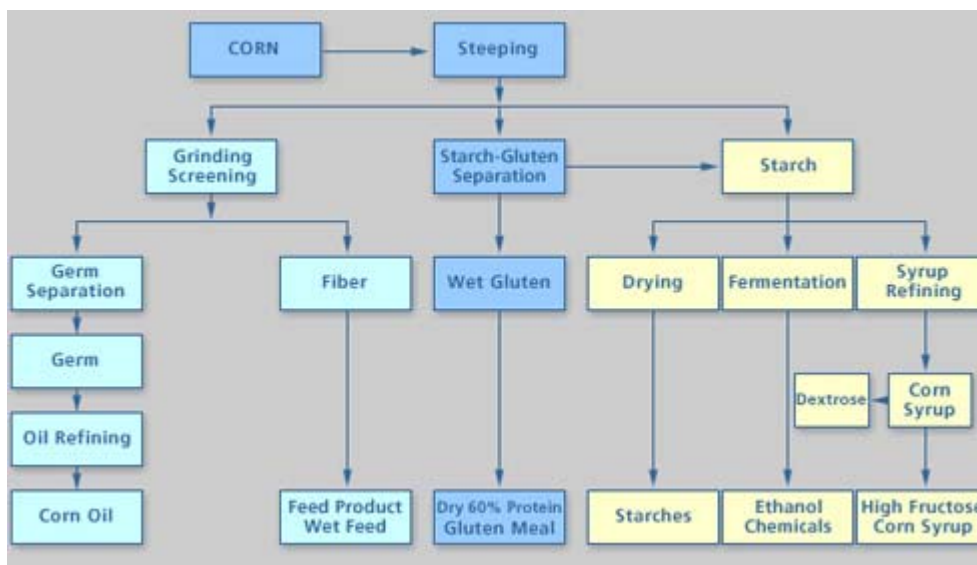
After steeping, the grain slurry is processed through a series of grinders to separate the germ portion of the kernel. In the case of corn, oil from the germ is either extracted on-site or sold to crushers who extract the corn oil. The remaining fiber, gluten and starch components are further segregated using centrifugal, screen and hydroclonic separators.

The steeping liquor is concentrated in an evaporator. This concentrated product, heavy steep water, is co-dried with the fiber component and is then sold as gluten feed to the livestock industry. Heavy steep water is also sold by itself as a feed ingredient or can be used in other applications such as a component in an environmentally friendly alternative to salt for removing ice from roads.

The gluten component (protein) is filtered and dried to produce the gluten meal co-product. This product is sought after as a feed ingredient in poultry broiler operations.

The starch and any remaining water from the mash can then be processed in one of three ways: fermented into ethanol, dried and sold as modified starch, or in the case of corn, processed into corn syrup. The fermentation process for ethanol is very similar to the dry mill process described above.

**Figure 25: Traditional Wet Milling Ethanol Production Process**



Source: Renewable Fuels Association

## Appendix C: Interview List

**Table 33: Interview List**

Company	Product/ Technology	Contact	Position
ORNL	General	Brian Davidson	Chief Scientist for Systems Biology and Biotechnology
NREL	General	Adam Bratis	Biochemical Platform Program Manager
NREL	General	James McMillan	Principal Chemical Engineer; Manager, Biorefining Process R&D
NCERC	General	John Caupert	Director
NCERC	General	Gene Peters	Process Engineering
Memphis BioWorks & Powell Consulting, LLC*	General	Randy Powell	AgBio Co-Coordinator / President
USDA, ARS,	General	Joseph Rich	Bioproducts and Biocatalysis Research, Research Leader
USDA, ARS	General	Cletus Kurtzman	Microbial Genomics and Bioprocessing Research, Supervisory Microbiologist
USDA, ARS	General	Julious Willett	Plant Polymer Research, Supervisory Chemical Engineer
USDA, ARS	General	Mark Berhow	New Crops and Processing Technology Research, Research Chemist
USDA, ARS	General	Sean Liu	Cereal Products and Food Science Research, Research Leader
USDA, ARS	General & Cellulosic Ethanol Biochemical Platform	Michael Cotta	Fermentation Biotechnology Research, Supervisory Microbiologist
USDA, ARS	Cellulosic Ethanol Biochemical Platform	Bruce Dien	Fermentation Biotechnology Research, Chemical Engineer
ButylFuel	Butanol	David Ramey	CEO
Gevo	Butanol	Dave Munz	Manager - Business Development
University of Illinois & Tetravita	Butanol	Hans M. Blaschek	Professor
Bioamber	Succinic Acid	Dilum Dunuwila	Business Development
BioProcess Innovations	Zein Extraction	Clark Dale	President
Cargill	3-HPA	Bill Brady	Media Relations
Vaperma	Ethanol Distillation - Membrane	Christian Roy	Founder and VP of Business Development
University of Minnesota	Anaerobic Digestion	Bill Lazarus	Professor
Prairie Gold	Zein Extraction	Oncor Patel	Project Engineer
MBI	Succinic Acid	Bernie Steele	Director of Operations

\*Previously served as the VP of Performance Chemicals Manufacturing for Eastman Chemical Company.