Asian J. Energy Environ., Vol. 3 Issues 1-2, (2002), pp. 27-51

Ethanol Production Technology in Thailand

Suthipong Sthiannopkao

Division of Environmental Technology
School of Energy and Materials
King Mongkut's University of Technology Thonburi

(Received : 10 April 2002 – Accepted : 10 October 2002)

Abstract : The use of ethanol as an alternative fuel source is presently a worldwide topic of discussion and research. As once abundant petroleum reserves dwindle and oil prices continue to rise, the search for alternative fuels becomes more intensive. Nowhere is this topic more relevant than Thailand, a country that imports 90% of the total amount of petroleum used each year. There are many reasons for Thailand to pursue an ethanol program designed to reduce dependence on fossil fuels in the transportation sector. The potential positive benefits of such a program for Thailand are well documented: relief of trade balance burdens due to heavy reliance on foreign oil, use of a potentially carbon neutral fuel, future national security, and rural economic stimulus. Such incentives have recently encouraged Thailand to consider ethanol production as a realistic opportunity to accomplish these goals.

Keywords : Ethanol production, Alternative fuel, Fermentation, Hydrolysis.

Production End

The face of ethanol production technology is old and ever changing. It is widely noted that centuries ago man discovered and began employing fermentation technology to produce alcohol; today ethanol is produced from a variety of materials for use as an industrial chemical and fuel. Through decades of research and development, the production of fuel ethanol has been developing throughout the world. Conventional processes have been maximized while advances continue to be made in lignocellulosic biomass conversion. Tried and true technologies such as acid and conventional enzymatic processes have been built upon through greater discovery and understanding of particular enzymes, advances in biotechnology and genetic engineering, more effective plant designs, and so on. In this section an attempt has been made to capture the essence of ethanol production as it pertains to Thailand through a basic review of some ethanol production processes including conventional technologies as well as some of the notable advances in the technology.

Conventional Process

Thailand currently operates a number of pilot-scale ethanol production facilities utilizing sugar cane or cassava feedstock. The

description that follows serves only as a representative of variable "conventional" fermentation-ethanol production processes. The technology and techniques are here termed conventional in relation to those some more advanced and less mature technologies and processes discussed later. This base example will include some elementary notes regarding ethanol production including the introduction of some terms and processes that will be referred to throughout the section.

To begin with, any fermentation process producing ethanol via fermentation requires a feedstock of some nature. Put simply, this feedstock may be sugar, starch, or lignocellulosic in nature. The feedstock must be pretreated and conditioned for fermentation according to its particular composition. For a solid, this usually includes some manner of grinding or chopping to produce very small pieces of the feedstock. If the material is not already a saccharide, i.e. starch, cellulose, or lignocellulose, it must then be hydrolyzed and saccharified. A saccharide is defined as a simple sugar or a more complex compound that can be hydrolyzed into simpler units. (http://www.ott.doe.gov/biofuels/glossary.html) Starch is generally defined as a polymer consisting of long chains of alpha-glucose molecules linked together (Figure 1).

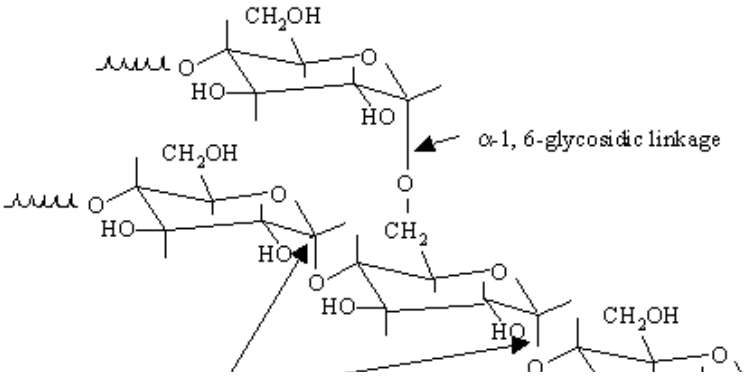

Figure 1. Structure of Starch (www.ott.doe.gov)**.**

The structure of starch tends to be amorphous and thus readily hydrolyzed to the simpler glucose disaccharide, maltose. Lignocellulosic material is more complex than starch. Such matter is composed of three main components, namely cellulose, hemicellulose and lignin. Generally the percentage composition of lignocellulosic biomass is as follows: 40-60% cellulose, 20-40% hemicellulose, and 10-25% lignin, depending on the biomass. Cellulose is also a polymer of glucose molecules, although linked in a different fashion. Units of $C_6H_{10}O_5$ are connected by β-glycosidic links that form linear and very stable chains that exhibit extensive hydrogen bonding, and when hydrolyzed split into the disaccharide celleboise (see Figure 2).

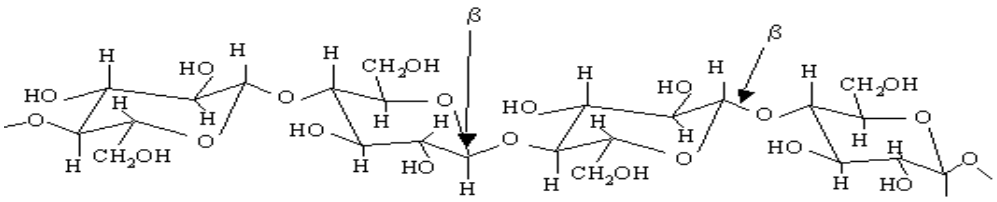

Figure 2. Structure of Cellulose (www.ott.doe.gov)**.**

For these reasons cellulosic material is significantly more resistant to hydrolysis than starchy material. Hemicellulose is a branched heteropolymer of not just glucose, but multiple five and six carbon sugars, such as the pentose sugars, D-xylose, L-aribinose, and the hexose sugars, D-galactose, D-glucose, D-mannose, L-rhamnos, and L-fuctose. The structure of hemicellulose varies with the particular biomass, but generally xylose constitutes a relatively large percent of the composition. Lignin is not composed of sugars, but is instead a complex aromatic polymer. As such, lignin cannot be used to make ethanol; however it can be utilized as a fuel source. (http://www.ott.doe.gov/biofuels/glossary.html; Zaldivar, 2001)

The example of "conventional" technology provided here illustrates the use of a solid starchy feedstock, such as corn. A basic outline of the important steps in the process from raw feedstock to ethanol is as follows:

I. Transportation of the feedstock.

II. Storage of the feedstock.

III. Grinding or chopping, etc. of the feedstock.

IV. Hydrolysis of the feedstock by cooking with water and malt or acid.

The prepared feedstock is cooked to gelatinize the material and allow the malt or acid to break down the starch to fermentable sugars. Generally well known enzymes, amylases, do the work.

V. Growth of inoculating cultures of yeast or bacteria.

During the starch conversion yeast is grown in a separate tank to be added to the fermentor along with the converted sugars.

VI. Fermentation.

The mash is fermented to beer with an alcohol content in the range of approximately 6% by volume to up to approximately 12% by volume.

VII. Distillation from beer.

VIII. The fermented broth is passed through heat exchangers, pumped to the top of a beer still, and as it passes down the column it separates. In the end stillage, consisting of residual sugar, protein, and maybe vitamins, leaves through the bottom and alcohol, water, and aldehydes remain as the overhead. The

overhead is passed through heat exchangers and then on to a dephlegmator. From here the condensate is sent to an aldehyde, or head, column for the separation of low boiling impurities.

IX. Rectification and purification of alcohol.

Finally, the alcohol is sent to the rectifying column where it is raised to approximately 95%.

X. Recovery of byproducts of process.

As mentioned earlier, the stillage contains protein, residual sugars, and possibly vitamins. This material may be dried and used as animal feed or fertilizer. Carbon dioxide created may also be sequestered and sold (Austin, 1984).

The above process serves as an appropriate foundation for the presentation of the current technology used in Thailand to convert cassava to ethanol. Fuel ethanol production in Thailand, although poised for commercialization, is still limited to the pilot plant scale. The Thailand Institute of Scientific and Technological Research (TISTR), developed an effective cassava to ethanol pilot plant almost twenty years ago. A recent visit to this particular plant indicated that the technology has changed little, if any, since the plant's construction and implementation in the early 1980's. The 1500 l/d capacity plant was used to examine both conventional fermentation and distillation processes, as well as a modified process that eliminates the cooking

step during hydrolysis and employed a pressurized variation of azeotropic distillation. Essentially the non-cooking hydrolysis is achieved using the same amounts of α-amylase and glucoamylase enzymes but allowing a longer reaction time. Together, these modifications greatly reduce steam demand and thereby save energy (Atthasampunna, 1987). Simpler still is the process for converting molasses to ethanol (see Figure 3). As discussed later, Thailand has abundant sugar cane, the processing of which results in molasses. Molasses vary in grade depending on the level of processing from which they result, but generally speaking molasses contain approximately 50-70% carbohydrates (sugars). Final molasses result when no more sugar can economically be removed and may contain approximately 35% sucrose as well as various percentages of other mixed sugars. Molasses can be fermented to alcohol using a traditional yeast, such as *Saccharomyces cerevisiae*.

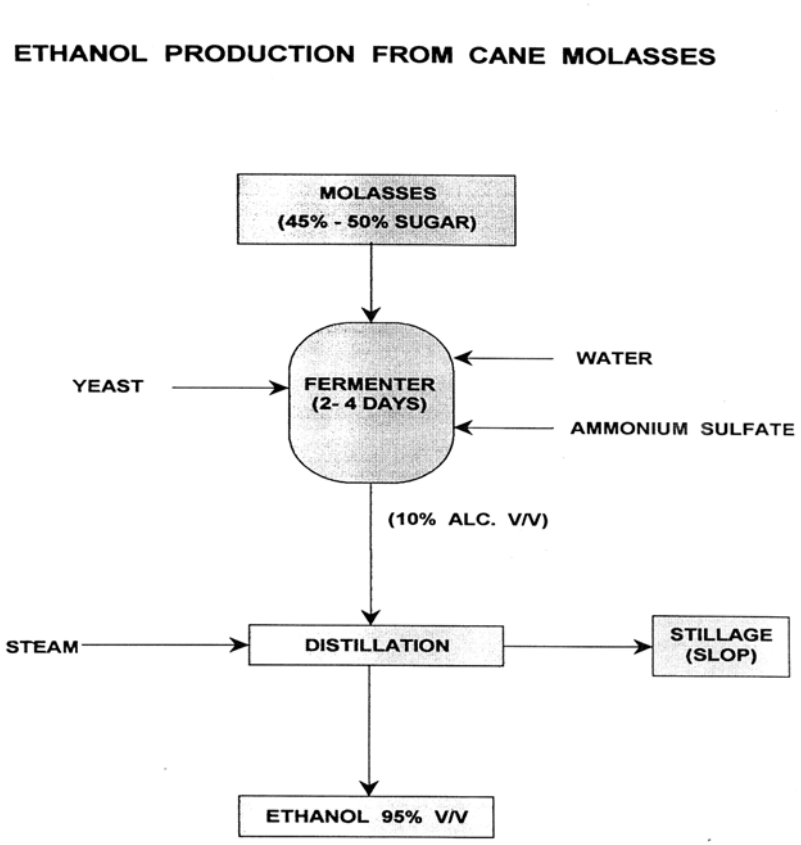

Figure 3. Ethanol from molasses (Scheitzer,1997).

Traditionally fermented alcohol can be distilled to 90-95.6% ethanol using a multi-column distillation process. The production of anhydrous, or pure ethanol, 99-99.9% is accomplished by removing the last 4-5% of water that remains. Various dehydration methods exist, including traditional azeotropic, membrane technology, and molecular sieve technology. Molecular sieves are crystalline metal aluminosilicates and are essentially special filters, which, as the name

implies, work at the molecular level. When hydrous ethanol passes through these special filters, the remaining water is adsorbed leaving nearly pure anhydrous alcohol (Scheitzer, 1997). To date molecular sieve technology is widely used and will be implemented at pilot plants in Thailand and most likely at the commercial scale as well. According to a personal communication with Khun Boonyipat (Nov. 2001), studies comparing the economics of differing distillation methods at various scales of production, molecular sieve technology seemed to be the most economical in terms of both investment cost as well as operating cost.

A Brief Review

Within the entire ethanol production process, the areas of greatest concern at present are the hydrolysis and fermentation steps. These steps are the most expensive process steps yet offer the greatest opportunity for cost reduction (Wyman, 1999). Furthermore, it is the initial steps in production, the hydrolysis and fermentation technology that dictates what feedstock may be used. For these reasons, the technological advances presented in this section are primarily concerned with these two areas of ethanol production. As described in the sample process above, the feedstock, if not saccharine in nature, must be saccharified.

Over recent decades intense research has been devoted to the development of efficient, cost effective production of ethanol from

cellulosic biomass. The greatest hurdle to leap is the conversion of such matter to fermentable sugars. The hydrolysis of cellulosic material into its constituents may be achieved through a variety of avenues. A 1994 report by the State of Hawaii includes a good comparative review of some lignocellulosic conversion technologies. This review has been used here to simply present the breadth of the technology. The report is now of course somewhat dated, as the field is ever changing, however for the purposes of this section the information remains relevant. All the information refers to the hydrolysis and fermentation steps of ethanol production. Traditional fermentation receives the least attention as it represents the most mature and well known process. The following brief descriptions have been adapted from the 1994 Hawaii report, and each is accompanied by a simple flow diagram.

Some hydrolysis processes utilize high heat and pressure to disrupt the lignocellulosic material. The process described hereafter was developed by Norval, in Canada. The biomass is prepared and then forced through steam at high pressure into a flash/recovery tank. When the pressure is decreased in this tank the auto hydrolysis of hemicellulose material occurs, together with a slurry of cellulose, hemicellolusic sugars, and melted lignin. The cellulose is then available for conversion and fermentation, the hemicellulose for fermentation, and the lignin for recovery (Figure 4).

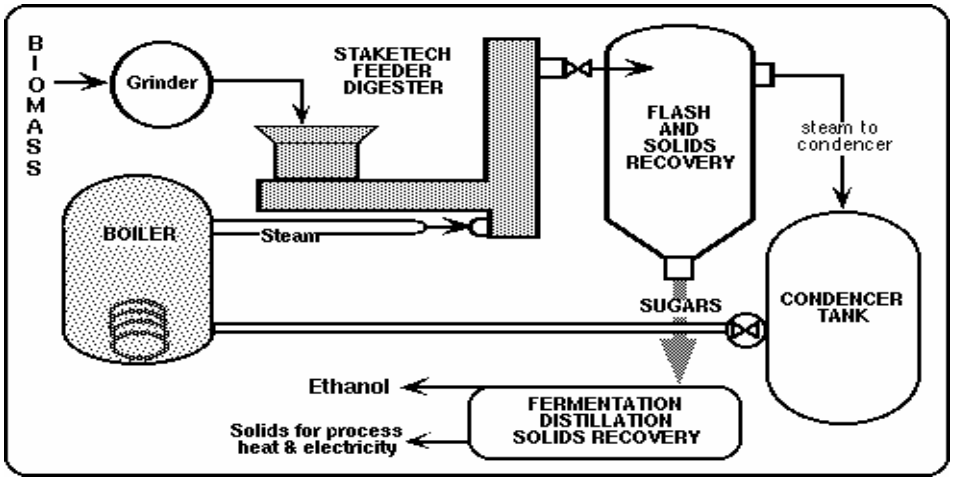

Figure 4. Steam disruption (Sheser,1994).

Another example employing an elevated temperature and pressure process involves treating the lignocellulosic material with acidified acetone at high temperature and pressure (see Figure 5).

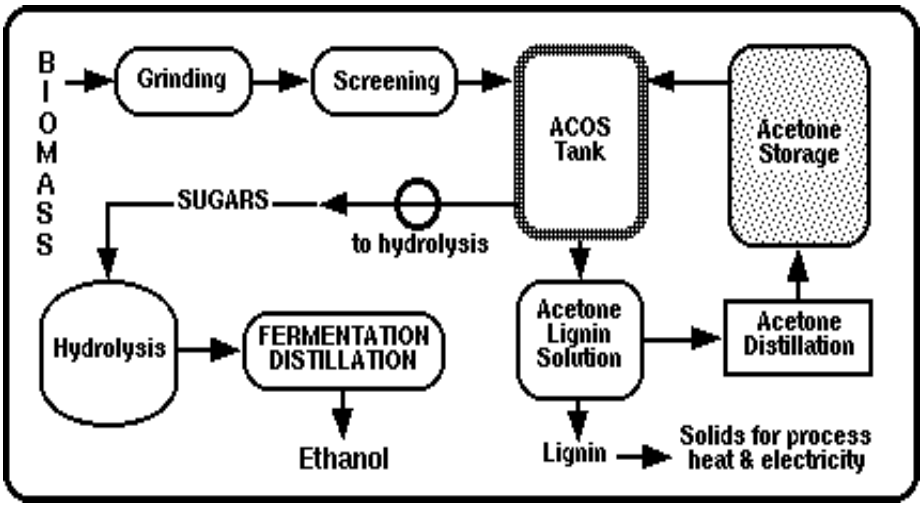

Figure 5. Acidified acetone hydrolysis (Shleser, 1994).

In ammonia disruption, ammonia is infused via high pressure treatment, causing the cellulose matter to swell and decrystalize. Upon release of the pressure, the matter explodes into a recovery tank where the cellulose and hemicellulose are readily converted to sugars and consequently fermented separately by employing appropriate yeasts (see Figure 6).

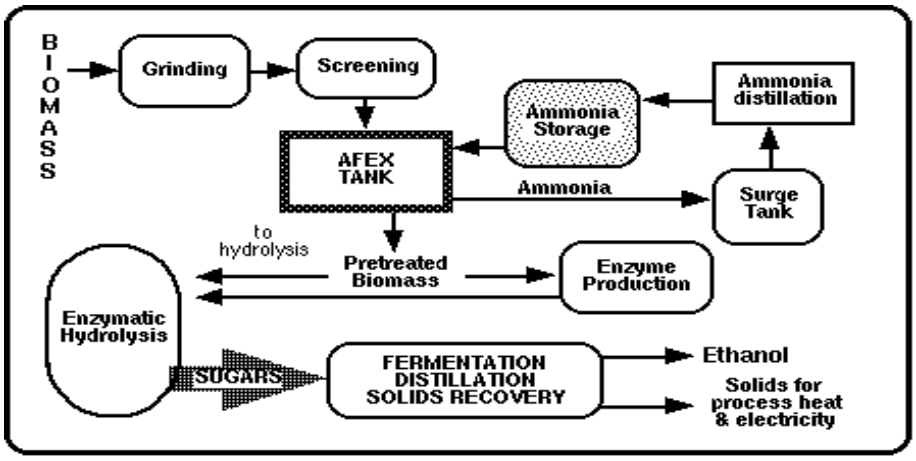

Figure 6. Ammonia hydrolysis (Shleser, 1994).

Some processes involve the use of acid to disrupt the lignocellulosic matter. This acid can be utilized in either dilute or concentrated forms to breakdown the biomass. The use of acid processes maintain the longest history and are regarded as effective, but in the past have not been economically viable except in specific economic environments, such as times of war. Now certain advances in the technology and processes have made acid hydrolysis processes

more attractive by reducing costs and boasting little detrimental environmental impact (Shleser, 1994).

Acid Hydrolysis Technology

Acid hydrolysis technology can trace its roots over a hundred years. In these processes acid is used to condition the biomass such that hemicellulose is converted to sugars and cellulose is susceptible to conversion by appropriate enzymes. Dilute acid hydrolysis saw its first attempt at commercialization in 1898 in Germany. The use of dilute acid was adopted by the US from German technology and through the years refined to an effective percolation process known as the "Madison Wood Sugar" process. This process spawned even further R & D and resulted in the development of dilute acid percolation reactors that still find use in Russia. Concentrated acid hydrolysis is nearly as old and has also been used commercially. The Japanese used membrane technology in 1948 to separate acid and the sugar, and during WWII, the USDA refined concentrated acid technology at its Northern Regional Research Laboratory in Peoria, Illinois. The process developed there, which came to be known as the Peoria Process, received attention again in the 1980's. Today companies are attempting to refine these processes for increasingly cost effective ethanol production by saving energy and limiting environmental impact. However, acid technology is reaching the limits of its potential after decades of development in greater sugar yields and more efficient processes. Different companies boast

different concentrations of acid, different temperatures, different durations of time, and so on with regards to the hydrolysis step. Generally speaking however, dilute processes tend to require higher temperatures than concentrated ones, and a greater amount of various by-products result from dilute concentration schemes (DOE/biofuels). The two examples provided here are based on technology developed by Arkenol and BC International Corporation. Both of these companies have developed advanced biomass to ethanol processes and are poised to construct commercial plants or are engaged in construction. Furthermore, both companies have expressed interest in Thailand, however, no information seems to indicate any investment in Thailand at this time.

Arkenol, a Nevada company based out of southern California, operates a pilot scale plant near it's corporate offices in Mission Viejo and plans to build a commercial scale plant for the conversion of rice straw. Because high concentration sulphuric acid is used, efficient recycling is extremely important to Arkenol's process. The company breaks down the cellulosic material into it's constituents, cellulose, hemicellulose, and lignin. The cellulose and hemicellulose are fermented separately and the lignin is removed to be utilized for fuel. Arkenol terms the thermal requirements of the process as "moderate" and seeks to build plants that use "waste" energy from power producing facilities. The use of the ethanol plant as a "thermal host" is one of the cost reducing factors that makes the overall process

economically viable. One relative benefit of concentrated acid technology is that there is relatively little degradation during the conversion of the biomass to fermentable sugars (www.arkenol.com) (see Figure 7).

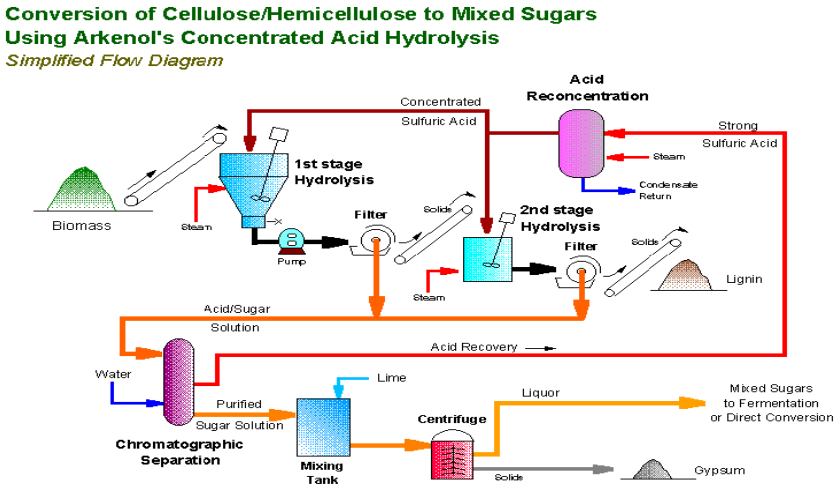

Figure 7. Arkenol flow diagram**.**

BC International Corporation, a private company in Dedham, Massachusetts, seeks to produce ethanol employing acid technology as well, however employing a dilute acid process. In addition, the company incorporates genetically engineered bacteria to ferment both hexose and pentose sugars resulting from the hydrolysis of biomass feedstock. The BCI process is founded upon the simplicity of traditional starch fermentation as illustrated by the flow diagrams below. The company hopes to shift to a fully enzymatic process, that is enzymatic hydrolysis and simultaneous saccharification and co-

fermentation, once the technology matures and becomes commercially viable (Gatto, 2000; www.bcintlcorp.com) (see Figure 8).

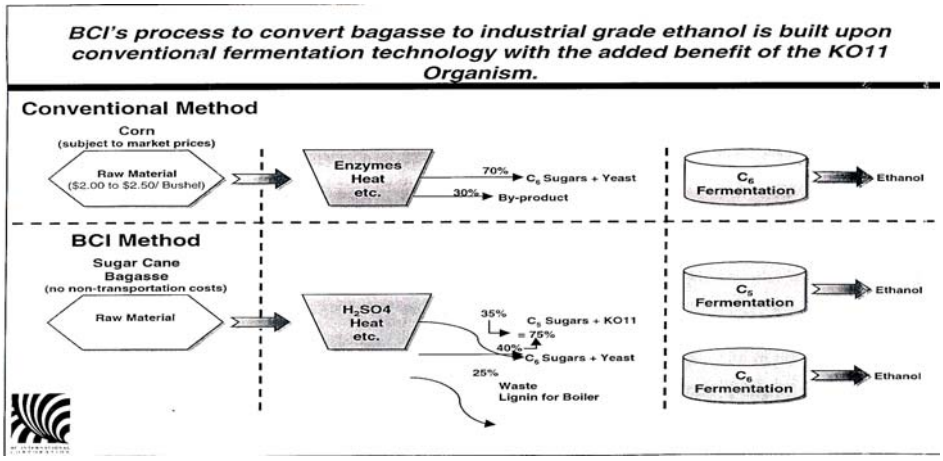

Figure 8. BCI simplified flow diagram (Gatto, 2000).

Another significant ethanol feedstock is municipal waste (MSW). The conversion of this material to fermentable sugars can also be achieved using acid technology. Masada Resource Group, LCC operates facilities that produce fuel grade ethanol from MSW.

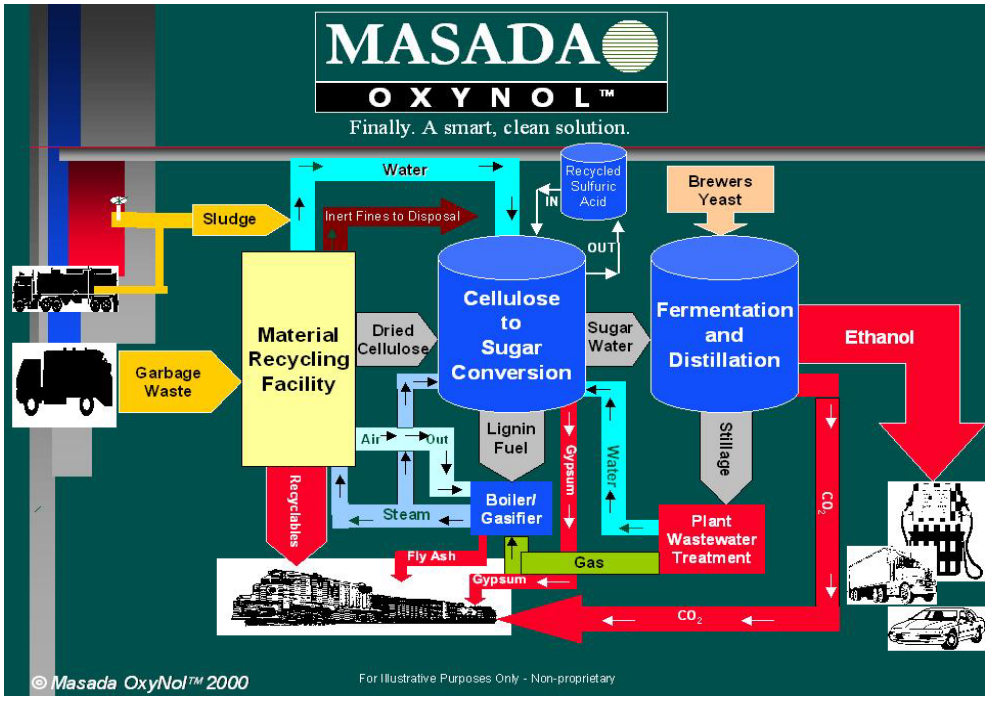

Figure 9. A simplified illustration of the Masada technology/process (http//:www.masada.com).

Waste is sorted, non feedstock material such as glass and plastic are recycled, while lignocellulosic material and other biomass is converted to fermentable sugars using acid hydrolysis technology. A commercial facility was scheduled for full operation in Middletown, New York in late 2001 or early 2002 (www.masada.com).

Enzyme Technology

The study of enzymes, often now referred to as cellulases, responsible for the break down of cellulosic biomass was intensified decades ago during WWII when the US army needed to understand the deterioration of fabric in the tropical climate of the South Pacific. The US Army Natick Laboratories were established in this effort to understand and curb cellulose hydrolysis. As a result of these studies the important cellulsase producing fungi *Trichoderma viride,* or as it came to be known, *Trichoderma reesei*, was consequently discovered. Cellulase research aimed at cellulose hydrolysis to achieve sugars for food or energy came into being in the mid 1960's when it was recognized that the cellulase enzymes could be prepared from fungal cultures. Such applications are still under intense research today as scientists try to develop enzyme "producers" best suited to ethanol production applications. Cellulase enzymes have been used in other industries, where smaller quantities are necessary and the final product is of greater value, such as stone washed denim (Sheenan, 1999). An important breakthrough in ethanol production from cellulosic biomass was the development of simultaneous saccharification and fermentation, often designated SSF. This achievement was important because it overcame a natural negative feedback mechanism in which cellulose conversion to glucose is inhibited by the very glucose produced. By saccharifying the cellulose and simultaneously fermenting the glucose produced, this negative feedback mechanism can be checked (Ingram, 1999). In addition, it literally can cut

equipment costs in half by eliminating the need for separate saccharification and fermentation vats associated with sequential processes. Another significant area of development involves microorganism engineering and development. As stated earlier, in addtion to cellulose, lignocellulosic hydrolysis produces five and six carbon sugars from hemicellulose, however, the traditional microorganisms used for crop-based ethanol production from fermentation, *S. cervisiae* and *Z. mobilis*, do not naturally metabolize five carbon sugars (Zaldivar, 2001). Work in genetic engineering has been and will continue to be the means to an end of the lignocellulose to ethanol predicament. The characteristics described as essential for enzyme producers are outlined below as adapted from Zaldivar, Nielsen, and Olsson (2001).

I. Ability to utilize all the simple sugars derived from lignocellulosic biomass.
II. Produce high ethanol yields and have high productivity.
III. Produce minimal fermentation by products such as glycerol and succinate.
IV. Have relatively high or increased ethanol tolerance.
V. Tolerance to inhibitors resulting from chemical pretreatment such as dilute acid hydrolysis.
VI. General hardiness and tolerance to fluctuations in process conditions such as pH or salts (Zaldivar, 2001).

Scientists have been able to engineer bacteria and create microorganisms which are “tailor-made” for producing ethanol from

complex biomass. In the US, National Renewable Energy Laboratory (NREL) scientists have made progress in the development of highly thermotolerant organisms as well as strains of xylose fermenting *Z. mobilis* (http://www.nrel.gov/technologytransfer/licenselist.html #biotech) Other genetically engineered organisms have the ability to ferment all the five carbon sugars and others have been designed to more efficiently convert and ferment cellulose. Ingram, *et al* (1999), at the University of Florida have created two such designated GMO's KO11 and P2. KO11 is a particular strain of *E. coli* bacteria that has been transformed using two specific genes from the bacteria *Z. mobilis*. This microorganism is capable of converting all the pentose and hexose sugars of hemicellulose. P2 was created from the bacteria *Klebseilla oxytoca* by inserting the same PET operon as in KO11. *K. oxytoca* naturally possesses the ability to ferment a wide range of monomeric sugars while also being capable of metabolizing celloboise and cellotroise, the products of enzymatic hydrolysis of cellulose. P2 is designed to convert cellulose and the resulting intermediates, celloboise and cellotroise, thereby reducing the need for extra fungal cellulases (Ingram, 1999). Enzyme technology and processes may be the most lucrative area for research and development; when compared to the other areas of ethanol technology, enzymes are the new frontier. This area of research and development exhibits great potential for further advances, and the cost reductions that can result from such advances are significant. Sheenan and Himmel (1999) project savings of $0.18 to $0.60 depending on the level of enzyme productivity and

activity. The field of enzyme development has increased by leaps and bounds in the past few decades, as has the field of biotechnology from which these developments arise. The progress thus far seems to indicate room for improvements and that these improvements are forthcoming.

Conclusion

At present Thailand produces ethanol at the pilot plant scale utilizing both cassava and sugar cane molasses. The technology employed for this production is conventional and proven. There is no doubt that in the near future Thailand can produce ethanol commercially utilizing this technology, as it is already produced in other parts of the world. At this time fuel ethanol production from lignocellulosic biomass exists at the commercial scale although it is not widespread, and not found in Thailand. Rather, existing commercial facilities produce for the industrial alcohol market, which is currently more lucrative. However, such technology seems to be moving towards greater commercialization; the advances reviewed in this section, particularly the progress in biotechnology, suggest the large-scale production of competitively priced fuel ethanol from various biomass sources is a real possibility in the near future. While bioethanol production in developed countries requires crops grown specifically for that purpose and substantial government subsidies, Thailand has an abundance of agricultural residues, such as rice hull/straw, sugar cane waste, cassava stalks, as well as feedstock

resulting from palm oil production and other biomass such as municipal waste, which have encouraging potential for producing ethanol. The key element being that residues and wastes are much cheaper than crop-based feedstocks, and feedstock costs account for a significant portion of total production costs. It is important to note that many aspects must come together to make these technological advances viable at the commercial scale. The information presented here only shows the tip of the iceberg, and developments in processes and materials exist in addition to the innovative hydrolysis and saccharification advances. However, until these technologies become more mature and increasingly economical it seems doubtful they will find a place in Thailand.

References

[1] www.arkenol.com

[2] Atthasampunna, P.; Eur-aree, A. (1987) Utilization of Cassava for Ethanol Production. *In* Upgrading of Cassava/Cassava Wastes by Appropriate Biotechnology. Bangkok, Thailand.

[3] Austin, G. (1984) Fermentation Industries. *In* Shreeve's Chemical Process Industries, J. Zseleczky (Ed.), 5th Edition, Mc Graw-Hill International Editions, Singapore, 578-601.

[4] www.bcintlcorp.com

[5] http://www.ott.doe.gov/biofuels/glossary.html

[6] Gatto, S. (2000) Ethanol From Biomass-The Next Generation. *Workshop on Biomass Derived Ethanol as Automotive Fuels in Thailand*, Bangkok, Thailand.

[7] Ingram. L. O. (1999) Enteric Bacterial Catalysts for Fuel Ethanol Production. *Biotechnology Progress*, 15, 855-866.

[8] Mielenz, J. R. (2001) Ethanol production from biomass: technology and commercialization status. *Current Opinion in Microbiology*, 4, 324-329.

[9] Sheenan, J.; Himmel, M. (1999) Enzymes, Energy, and the Environment: A Strategic Perspective on the U.S. Department of Energy's Research and Development Activities for Bioethanol. *Biotechnology Progress*, 15, 817-827.

[10] Scheitzer P. A. (1997) *Handbook of Separation Techniques for Chemical Engineers.* Mc Graw-Hill.

[11] Shleser, R. (1994) Ethanol Production in Hawaii. Prepared for the State of Hawaii, Department of Business, Economic Development and Tourism. Honolulu: Energy Division, Dept. of Business, Economic Development and Tourism, State of Hawaii, 1. Energy crops-Hawaii. 2. Alcohol as fuel-Hawaii. 3. Biomass energy-Hawaii. HD9502.5.B54.S4.

[12] Wyman, C. (1999) Biomass Ethanol: Technical Progress, Opportunities, and Commercial Challenges. *Annual Review of Energy and the Envionment*, 24, 189-226.

[13] Zaldivar, J.; Nielsen, J.; Olsson, L. (2001) Fuel ethanol production from lignocellulose: a challenge for metabolic engineering and process integration. *Applied Microbiology and Biotechnology*, 56, 17-34.