**XVII**th **World Congress of the International Commission of Agricultural and Biosystems Engineering (CIGR)**

Hosted by the Canadian Society for Bioengineering (CSBE/SCGAB)
Québec City, Canada June 13-17, 2010

# ENERGY ANALYSIS OF BIOCHEMICAL CONVERSION PROCESSES OF BIOMASS TO BIOETHANOL

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**CSBE101214 – Presented at the Section IV: Rural Electricity and Alternative Energy Sources Conference**

**ABSTRACT** Bioethanol is one of the most promising biofuels that can replace or compliment fossil fuels. It is a renewable resource that can be produced from different biomass including agricultural products, waste and byproducts. In this paper, energy analysis for conversion of different groups of biomass including lignocelluloses, starchy and sugar biomass to bioethanol were studied. Depending on the structure of a biomass, biochemical conversion typically involves the breakdown of the biomass to simple sugars using different pretreatment methods. Energy requirement for the various conversion steps were calculated and summed to obtain mass and energy efficiencies for the conversions. Mass conversion ratios of corn, molasses and rice straw were calculated as 0.3396, 0.2300 and 0.2296 kg of bioethanol per kg of biomass, respectively. The energy efficiency of biochemical conversion of corn, molasses and rice straw were calculated as 28.57, 28.21 and 31.33%, respectively. The results show that conversion of lignocelluloses with specific microorganisms such as *Mucor indicus*, *Rhizopus oryzae* and using the Simultaneous Saccharification and Fermentation (SSF) methods or similar technologies is very attractive for many reasons.

**Keywords:** Biofuels, Bioethanol, Fermentation process, Lignocellulose biomass, Starchy Biomass, Sugar Biomass, Biochemical energy conversion efficiency.

## INTRODUCTION

The sun provides the majority of energy on earth through solar radiation. Solar energy is a result of nuclear fusion reactions within the sun and this energy radiates to the earth over a range of wavelengths of electromagnetic energy that we know as light and heat. This light energy is harnessed naturally by plants through photosynthesis to create a portable source of energy in the form of complex carbon, hydrogen, and oxygen compounds called sugars and carbohydrates. This chemical and physiological process of photosynthesis can be modeled as follows:

$$n\,(6\,CO_2 + 5H_2O) \qquad (C_6H_{10}O_5)n + n\,6O_2 \tag{1}$$

Where *n* is the polymerization factor.

Glucose is the simplest form of carbohydrates with $n = 1$ and is the easiest to convert to bioethanol. Starch an important human and animal carbohydrate diet compose of approximately 25% amylose and 75% amylopectin by mass. Amylose is a polymer with $n = 300 – 3,000$ repeating glucose units, while amylopectin is a polymer with $n = 2,000 – 200,000$ glucose units (Lakatos and Handki 2008). Lignocellulose is the most complex and the most abundant biomass. It is comprised of three main chemical building blocks: cellulose $[(C_6H_{10}O_5)_n]$, hemicelluloses $[(C_5H_8O_4)_n]$, and lignin $[C_9H_{10}O_3.(OHCH_3)_{0.9\text{-}1.7}]_n$ . These building blocks make up the structural part of plants and are intertwined (figure 1) making lignocellulose difficult to convert to bioethanol. To date, the commercial production of bioethanol from lignocellulose is still at its infant stage. The data used for this analysis is based on experimental, empirical and pilot scale results.

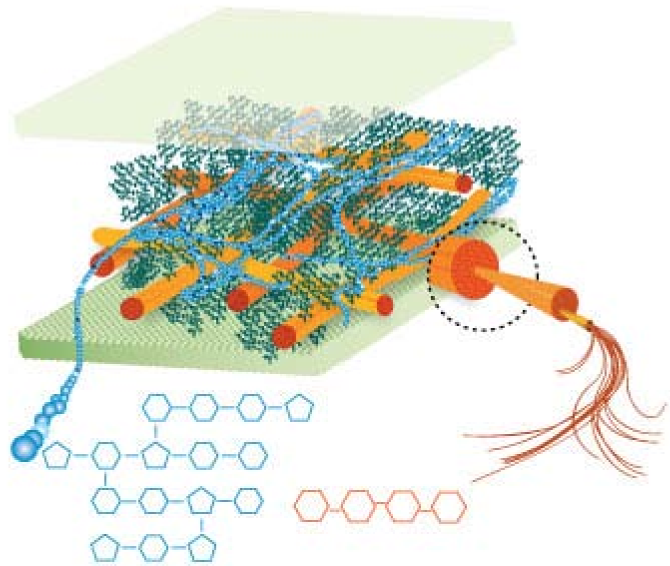

Figure 1: Complete molecular structure of biomass containing all the three main components with cellulose is shown in orange, the hemicelluloses in blue, and the lignin in green (IATA 2009 Alternative Energy Report; Ceres Biofuels)

The production of bioethanol centers on bioconversion of sugars to ethanol in a process known as fermentation with the aid of microorganisms. *Saccharomyses cerevisiae* known as the bakers' yeast has been the traditional and an effective organism for bioconversion of simple sugars to bioethanol.  For complex biomass, pretreatment is a necessary process.  This process helps to break down the complex sugar to simpler forms that can be fermented by *S. Cerevisiae*.  However, other microorganisms such as *E. coli, Mucor indicus, Rhizopus oryzae, Candida shahatae, Pichia stipitis* are more effective in producing bioethanol from complex biomass such lignocelluloses than *S. Cerevisiae* alone. Enzymatic and thermochemical processes can also be used for the production of bioethanol.  The viability of production process of bioethanol from biomass depends on whether it is:

- Energy efficient with a positive net energy value (NEV) when the energy input during process is compared with the energy content of the bioethanol produced.
- Mass efficient, with low non-reusable byproducts.
- Cost effective with available technology and human resources.
- Environmentally friendly with a positive net environmental effect (NEE).

In this paper, energy analysis for conversion of different groups of biomass including lignocelluloses, starchy and sugar biomass to bioethanol were studied.

## MATERIALS AND METHODS

Established biochemical conversion technologies of the three group of biomass namely, sugar based, starchy based, and lignocelluloses were investigated. Detailed efficiency analysis was carried out based on published experimental and empirical data. The energy requirement for the various conversion steps were calculated and summed to obtain mass and energy efficiencies for the conversions. The parameters used to determine the efficiencies are as defined below. The advantage of using these parameters is to enable comparison between biochemical conversions of biomass to bioethanol to other conversion processes such as thermochemical conversions.

### Definition of parameters

Mass Ratio: The mass ratio of the bioethanol is defined as the mass of the bioethanol produced and the mass of the biomass feedstock that is used:

$$Mass\ ratio = \frac{Mass\ of\ the\ Bioethanol}{Mass\ of\ the\ biomass\ feedstock} \tag{2}$$

Net Energy Value (NEV)

NEV is the difference between the energy in the bioethanol and the process energy that was required to produce the fuel from 1 kg of the biomass:

$$NEV = Energy\ of\ the\ produced\ bioethanol - net\ process\ energy \tag{3}$$

Process Energy Ratio

This is the ratio between the energy in the bioethanol and the process energy that was required to produce the fuel:

$$Process\ energy\ ratio = \frac{Energy\ in\ \ Bioethanol}{Process\ Energy} \tag{4}$$

Energy Ratio

This is the ratio between the energy in the bioethanol and the energy of the original biomass feedstock from which the fuel is produced**:**

$$Energy\ ratio = \frac{Energy\ of\ Bioethanol}{Energy\ in\ \ biomass\ feedstock} \tag{5}$$

Energy Efficiency

This can also be referred to as 1st order efficiency, it is the ratio between the energy in the bioethanol and the sum of the energy of the original biomass from which the fuel is produced plus the process energy**:**

$$Energy\ efficiency = \frac{Energy\ in\ bioethanol}{Energy\ in\ biomass\ feedstock + Process\ Energy} \times 100\% \quad (6)$$

**Biochemical conversion of lignocellulose biomass to bioethanol**

Lignocellulose biomass is the most abundant and least utilized biomass for the production of bioethanol due its structural complexity that inhibits fermentation. Lignocelluloses include corn stover, wood sawdust, switch grass, wheat straw, rice straw, etc. In this study the energy analysis of the conversion of rice straw to bioethanol is presented. Rice straw is one of the most abundant lignocellulosic agricultural wastes with the annual production of 600 million tons per year (Abedinifar et al, (2009)).

The conversion of rice straw and other lignocellulose biomass to bioethanol is more complex than the production of ethanol from other agricultural product, such as starch and sugars. The structure of all lignocellulosic biomass consist of cellulose $(C_6H_{10}O_5)]_n$, hemicelluloses such as xylan $(C_5H_8O_4)$, and lignin $[C_9H_{10}O_3.(OHCH_3)_{0.9-1.7}]_n$ in trunk foliage and bark. The complex arrangement of these structural components makes it difficult to convert the cellulose and hemicelluloses to sugars and ultimately bioethanol biochemically or thermochemically. Table 1 gives the proportion of these structural components in treated and untreated rice straw (Abedinifar et al, (2009)).

Table 1. Composition of untreated and pretreated rice straw with steaming or dilute-acid

| Pretreatment of rice straw | Hemicellulose (%) | Cellulose (%) | Lignin (%) | Ash |
|---|---|---|---|---|
| No treatment | 24 ± 0.8 | 38 ± 0.7 | 8 ± 0.4 | 15 ± 1 |
| Steam | 2 ± 0.3 | 51 ± 0.5 | 7 ± 0.4 | 13 ± 1 |
| Dilute Acid | 1 ± 0.4 | 55 ± 0.3 | 5 ± 0.3 | 13 ± 0.2 |

The abundance of lignocellulose biomass such as rice straw have motivated extensive research on the development of effective process of converting lignocellulose bioethanol. Most of these processes are either at the experimental or pilot scale stages. The advanced established processes as shown in figure 2 include Simultaneous Saccharification and Fermentation (SSF), and Simultaneous Saccharification and Co-Fermentation (SSCF).

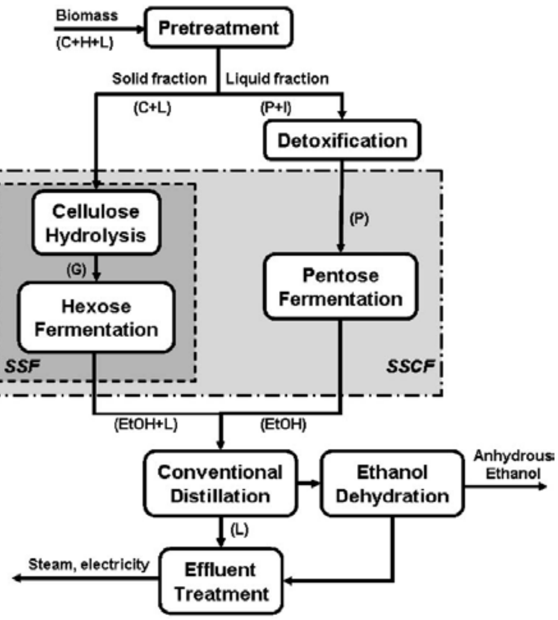


Figure 2. Generic block diagram of bioethanol production from lignocellulose biomass (Cardona Alzate and Sanchez Toro (2005))

Regardless of the method chosen, the following features must be assessed in comparison with established sugar or starch based bioethanol production:

- Efficient de-polymerization of cellulose and hemicellulose to soluble sugars.
- Efficient fermentation of a mixed sugar hydrolysate containing six carbon (hexoses) and five carbon (pentoses) sugars as well as fermentation inhibitory compounds.
- Advanced process integration to minimize process energy demand.
- Lower lignin content of feedstock decreases the cost of Bioethanol, although the separated lignin can increase the renewability of the bioethanol if it is used as fuel for powering the process boilers.

Considering the above points, the processing of bioethanol from lignocellulose materials such as rice straw will include the following process:

1. Raw Stock preparation by milling the rice straws to an optimum size to facilitate effective pretreatment.
2. Pretreatment of the milled rice straw to facilitate effective Hydrolysis and fermentation.
3. Hydrolysis that will involve effective conversion of cellulose to sugars, with the minimization of fermentation inhibiting substances like furfurals.
4. Fermentation which will involve the effective biochemical conversion of both the 6 and 5 carbons sugars to bioethanol by one organisms as in the case of SSF or two organism as in the case SSCF.
5. Purification through Filtration and/or distillation to remove the by-products from the Bioethanol.
6. Waste by-product management, which includes effective utilization of lignin and the other components for generation of energy.

Pretreatment is a critical stage in the process because it facilitates the separation of the three main structural components namely cellulose, hemicellulose, and lignin. Effective pretreatment enables the microorganism to convert the sugars to bioethanol, and it enables the process to utilize the lignin and other waste to generate a large portion of the energy that the process requires.

Fermentation process requires the selection of the fermenting microorganisms. The microorganisms' ability to convert the sugars to bioethanol determines the yield of the process. In SSCF process, two microorganisms are used, one (e.g. *Saccharomyses Cerevisiae*) to convert the six-carbon sugars (hexose) and the other (e.g. *Candida shahatae* or *Pichia stipitis*), to convert the 5-carbon sugars (pentose) to bioethanol. In the SSF process a microorganism that is capable of converting both the hexose and pentose such as *Mucor indicus*, or *Rhizopus oryzae* is used for fermentation.

Karimi et al (2006) reported that 1 kg of rice straw with the cellulose extraction efficiency of 73.58% and hemicellulose extraction efficiency of 77% will produced .226g of bioethanol using R. oryzae and the Simultaneous Saccharification and Fermentation (SSF) method. Utilizing this information and the energy analysis flowsheet that was generated by Cardona Alzate and Sanchez Toro (2006), Maas et al (2008), and other literature that are listed, the mass efficiency, NEV, process energy ratio, energy efficiency were calculated for rice straw calculated. The efficiency of conversions of the cellulose and hemicellulose conversion was assumed to as Karimi et al (2006) had predicted and the microorganism assumed for the fermentation using SSF process is *Rhizopus oryzae*.

<u>Summary of the process energy requirement</u>

The total energy consumption and the sub-processes energy consumption of converting 1 kg of rice straw to bioethanol is as shown in table 2:

Table 2. Process energy consumption of converting 1 kg of rice straw to bioethanol

| Process step | Energy consumption MJ/kg | Energy recovery MJ/kg |
|---|---|---|
| Pretreatment & SSF | 1.23 | |
| Distillation | 8.00 | |
| Evaporation | 2.21 | |
| Effluent treatment | 0.79 | |
| Released biogas | | 1.85 |
| Burned lignin | | 9.49 |
| Electricity credit | | 0.47 |
| Feedstock handling | 0.31 | |
| Transportation | 0.33 | |
| Total net | 1.05 | |

## Biochemical conversion of starchy biomass to bioethanol

Grains such as wheat and corn have been used to produce bioethanol in Asia, Europe, and the Americas. The only issue is the competition between food and fuel. The production process of bioethanol from grains is much simpler than from lignocellulose biomass. Grains contain between 50 to 67% starch. The biochemical process of converting grains into bioethanol includes the grinding of the corn, hydrolysis, fermentation, distillation, dehydration and effluent treatment. In this section, energetic analysis of the processing of bioethanol from corn is presented. If we consider equation on molar basis neglecting the polymerization factor which does not affect the energetic analysis in this case. The equation can be written as:

$$264\ kg\ CO2 + 90 kg\ H2O \xrightarrow{\text{Photosynthesis}} 162\ kg\ Starch + 192\ kg Oxygen \quad (7)$$

Grinding of the Corn

The grinding of corn usually involves a milling machine that is diving by an electric motor. If we consider 1 kg of corn of dry corn is grounded by the milling machine to the desired size of 20 size sieve (833μm). The energy utilization according to Kim and Dale (2005) is 0.8 percent of the total energy requirement for processing the corn to ethanol. Also considering that the amount of starch in the corn is 65% per mass, we will have 0.65 kg of grounded starch.

Pretreatment of the Corn

The objective of this process is open up the starch of the corn so as fermentation process will occur. The pretreatment process involves Hydrolysis, Dilute acid medium, heat, and addition of amylase enzymes.

For each molecule of starch, one molecule of water is added and this gives one molecule of sugar as is shown in equation 8:

$$(C_6H_{10}O_5)n + n\ H_2O \qquad n\ C_6H_{12}O_6 \quad (8)$$

Considering the molar masses and writing equation (8) for 0.65 kg of Starch (1 kg), we have:

$$0.650\ kg\ of\ Starch + 0.072\ kg\ of\ Water \qquad 0.722 kg\ of\ Fermentable\ Sugar \quad (9)$$

The pretreatment process involves mixing the ground corn (meal) with water and partially disinfecting it at a temperature of about 105 degrees- and a pressure of 0.7-2 bars. This is followed by cooking at a temperature of about 82-90 C for 4-8 hours. The first enzyme called alpha-amylase that breaks the starch into individual molecules of sugar is added during liquefaction and the second enzyme called Gluco-amylase either during saccharification or at the beginning of fermentation. The total energy input for this process includes the energy requirement of the water pump, mixer, heater, enzyme pump, meal, and auxiliary equipment energy. It has been reported that this energy as a percentage of the total energy requirement of the process is about 29 percent [Kim and Dale, 2005].

Fermentation

This biochemical process involves the use of yeast (*S. cerevisiae*) which breaks down the sugar into bioethanol, carbon dioxide and heat. The fermentation time is usually around 54 hours and highly dependent on the metabolic characteristics of the microorganism used, the amount of enzyme and the fermentation temperature. Considering 1kg of corn which gives fermentable sugars of 0.722 kg with the current microorganisms and fermentation technology of 92% efficiency, 0.3396 kg of bioethanol will produced. The reported fermentation energy input requirement is between 4.1% of the overall energy requirement.

Distillation and Dehydration

After the fermentation process is complete, the heavy liquid with solid particles called beer is pumped into multi-distillation column system that removes bioethanol from the beer by heating the liquid above the boiling point of bioethanol which is 78 ºC and below the boiling point of 100 ºC. The boiled bioethanol is condensed at the top of the column and collected and transferred to the dehydration unit which is the final dewatering process. Distillation process consumes the major amount of energy in the biochemical ethanol production process. It consumes 56.5% of the overall energy consumption for dry corn milling and fermentation process.

Summary of the process energy requirement

The total energy consumption and the sub-processes energy consumption of converting 1 kg of corn to bioethanol is as shown in table 3.

Table 3. Process energy consumption of converting 1 kg of corn to bioethanol

| Sub-process | % Energy consumption | Process Energy (MJ/kg of corn) |
|---|---|---|
| Grinding | 0.80% | 0.042 |
| Pretreatment | 29% | 1.512 |
| Fermentation | 4.1% | 0.182 |
| Distillation | 56.50% | 2.946 |
| DDGS recovery | 9.60% | 0.501 |
| Total | 100% | 5.183 |

## 2.4 Biochemical conversion of sugar biomass to bioethanol

The production of bioethanol from sugar containing agricultural products is less complicated. The sugar is in the form that the microorganism can attack and digest without undergoing extensive pretreatment. During sugar production whether it is using sugar beets as is the case in Europe or whether it is using sugarcane as is the case in tropical and subtropical regions. Molasses a byproduct of the process contains a high percentage (42 %) of sugar that can be used to produce bioethanol. Another advantage is that the other byproducts such as baggase in the case of sugar processing from sugarcane can be used as thermal energy source for the process. The benefit of this multiple gain appreciates with the size of the plant and the proximity of the plant to the sugarcane plantation. The energy analysis of the biochemical energy conversion molasses to bioethanol using data from 100,000 L/day plant was carried out. This is based on a study that was carried out in India by Prakash et al (1998). Table 5 shows process energy requirements for converting 1 kg of molasses to Bioethanol.

<u>Summary of the process energy requirement</u>

The total energy consumption and the sub-processes energy consumption of converting 1 kg of molasses to bioethanol is as shown in table 4**.**

Table 4. Process energy consumption of converting 1 kg of molasses to bioethanol

| Process step | Energy consumption MJ/kg | Energy recovery MJ/kg |
|---|---|---|
| Fermentation | 0.252 | |
| Distillation | 2.004 | |
| Dehydration | 0.816 | |
| Effluent treatment | 0.553 | |
| Auxiliary equipment | 0.036 | |
| Energy released Biogas | | 1.904 |
| Total net | 1.757 | |

**RESULTS AND DISCUSSION**

Table 5 shows the summary of the performance parameters of the biochemical conversion of lignocellulose, starchy, and sugar biomass, of the rice straw, corn, and molasses respectively. From this table can be that corn has the highest mass ratio but has lower first order energy efficiency than rice straw through the SSF process and about comparable efficiency with molasses. This can be attributed to the lignin content of the straw that is used as fuel for powering the process. In a thermochemical conversion process through pyrolysis and gasification, the efficiency of converting rice straw to bioethanol is even much higher because the lignin is used directly as part of the conversion process.

Table 5. Performance parameters summary of the three groups of biomass

| Biomass | Mass ratio | NEV | Process Energy Ratio | Energy ratio | Energy efficiency |
|---|---|---|---|---|---|
| | | MJ/kg | | | |
| Rice straw | 0.2296 | 4.323 | 5.117 | 0.3337 | 31.33% |
| Corn | 0.3396 | 2.730 | 1.520 | 0.3516 | 28.57% |
| Molasses | 0.2300 | 3.625 | 3.063 | 0.3107 | 28.54% |

**CONCLUSION** Utilization of the abundant lignocellulose biomass as the source of producing bioethanol through biochemical process is very attractive. This study has shown that with the experimental and pilot scale data, rice straw is still more efficient than utilizing corn that is also used as food source for ethanol production. The adoption of mass-based parameters that focus on the biomass feedstock rather than the bioethanol produced will enable comparative analysis between biochemical conversion and other conversion process such as thermochemical conversion. Also these parameters can be used to effectively optimize the bioconversion process steps based on the feedstock potential.

**Acknowledgements.** The authors appreciate the support by the International Air Transportation Agency (IATA) for the IATA-McGill 2nd Generation Biomass Conversion Efficiency project and the IATA 2009 Reports on Alternative Fuels which have contributed a great deal towards this publication. The authors would also like to thank all the experts who have contributed immensely ensuring that the project is successful.

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