

HYDROLYSIS OF LIGNOCELLULOSIC BIOMASS

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INTRODUCTION

The production of liquid biofuels from lignocellulosic biomass can significantly reduce the world dependence on oil, so it has become a research area of great interest to many governments, academic groups and companies.

Today it is possible due to advances in agriculture and biotechnology to propose the inexpensive production of biofuels, especially bio-ethanol based on lignocellulosic biomass as well as other biomass feedstocks.

So far, Brazil² and USA⁴ have made significant advances in the production and use of bioethanol, in the first case derived from sugarcane (currently 15 billion liters of ethanol are produced) and the second uses corn (for 2017 it is expected to reach a production of 132 billion of liters). This situation has caused a controversy in the use of soil, water and other resources between food *vs* energy. For this reason in several parts of the world, in universities and companies, there are research programs trying to understand the best way to use lignocellulosic materials for production for bioethanol and other biofuels.

Abundant and inexpensive lignocellulosic biomass does not compete with the production of food crops. Economically, lignocellulose has an advantage over other agriculturally important biofuels feedstocks such as corn starch, soybeans and sugarcane because it can be produced quickly and at significantly lower cost than food crops. Lignocellulosic biomass is also an important component of the major crops already mentioned; it is

the non-edible portion of the plant, which is currently underutilized but could be used for biofuels production.

Availability of lignocellulosic biomass is not in general a limitation in most parts of the world. For example, USA has a large amount of underutilized biomass, Table 1. In fact, non-food biomass, including trees, grasses and agricultural residues, constitutes more than 80% of the biomass; in 2005 it was estimated that 1.3 billion dry tons of this non food biomass could be available for large scale bioenergy and biorefining industries by the middle of the 21st century. This much biomass has the energy content of 3.8 billion barrels of oil; an amount equivalent to approximately half the oil consumed in that country in 2006.

Lignocellulosic biomass feedstocks for biofuels production can be derived from both, forest and agricultural resources. Forest resources include residues such as tree bark and scrap wood and urban wood residues consisting mainly of municipal solid waste. Agricultural resources consist mainly of crop residues, which are mostly leaves and stems (v. gr. corn stover), from crops grown for food and fiber such as sugarcane, soybeans, corn and wheat. Additionally more recently several researchers have proposed grasses (v. gr. switch grass) and fast-growing trees (v. gr. poplar) to be considered specifically for bioenergy.

The key bottleneck for the use of lignocellulosic biomass as raw material to obtain biofuels is the lack of technology for the efficient conversion of biomass into liquid fuels. The limiting factor is simply that low cost processing technologies to effi-

TABLE 1 Potential USA biomass resources⁴.

Biomass	Million dry tons per year
Forest biomass	
Forest products industry residues	145
Logging and site-clearing residues	64
Forest thinning	60
Fuetwood	52
Urban wood residues	47
<i>Subtotal for forest residues</i>	368
Agricultural biomass	
Annual crop residues	428
Perennial crops	377
Misc. process residues, manure	106
Grains	87
<i>Subtotal for agrocltural resources</i>	998
Total biomass resource potential	1,366

ciently convert a large fraction of the lignocellulosic biomass energy into liquid fuels do not yet exist.

A comprehensive understanding of the fundamental chemistry, science and engineering underpinning the chemical transformation of lignocellulosic materials into biofuels is necessary to build on the many advances that have already been made in the development of bio-ethanol production processes.

For the transformation of lignocellulose into bio-ethanol, several steps are needed: collection of lignocellulosic biomass, a pretreatment stage, a hydrolysis stage to obtain sugars from cellulose and hemicellulose present in biomass, conversion of sugars into bioethanol by fermentation and elimination of water in the biofuel in order to reach the technical specifications required.

In this paper I present a review of the state of art of one of these stages: hydrolysis of lignocellulosic biomass. But before doing so, some comments will be made about what are the main components of lignocellulosic materials and what it is known about its chemistry and structural composition.

BIOMASS AS RAW MATERIAL

Lignocellulosic is much more difficult to convert into ethanol than sugars, starches and oils. Lignocellulose is the fibrous material that forms the cell walls of the plants "architecture", It consists of three major components, Figure 1:

- Cellulose, which consist of high molecular weight polymers of glucose that are held rigidly together as bundles of fibers to provide material strength. The cellulose typically accounts for some 40 wt% of the lignocellulose.
- Hemicellulose, which consists of shorter polymers of various sugars that glue the cellulose bundles together. It usually accounts for some 25 wt% of the lignocellulose.
- Lignin, which consists of a tri-dimensional polymer of propyl-phenol that is imbedded in and bound to the hemicellulose. It provides rigidity to the structure. It accounts for some 20 wt% of the lignocellulose.

In Table 2, it is shown some of the main resources of lignocellulose and their chemical composition in terms of cellulose, hemicellulose and lignin. It can be appreciated that the potential of sugar production in most of them vary from 60-70% that is 600-700 Kg of sugar/ton of dry lignocellulosic material. Also in Figure 1 there is a representation of structure and attachment that are between the three polymers: lignin occludes polysaccharides and for that reason it is necessary to remove it.

Due to this difficulty in structure several production processes have been developed, in Figure 2, three of them are shown. All try to explore different options looking for better yields and lower cost of processing:

- a) The conventional thermochemical route to biofuels brakes down starch (or other biomass) into a mixture of carbon monoxide and Hydrogen. This mixture is then converted catalytically into synthetic diesel.
- b) Conventional biological routes convert starch to Glucose, which is then fermented by microorganisms to produce ethanol.

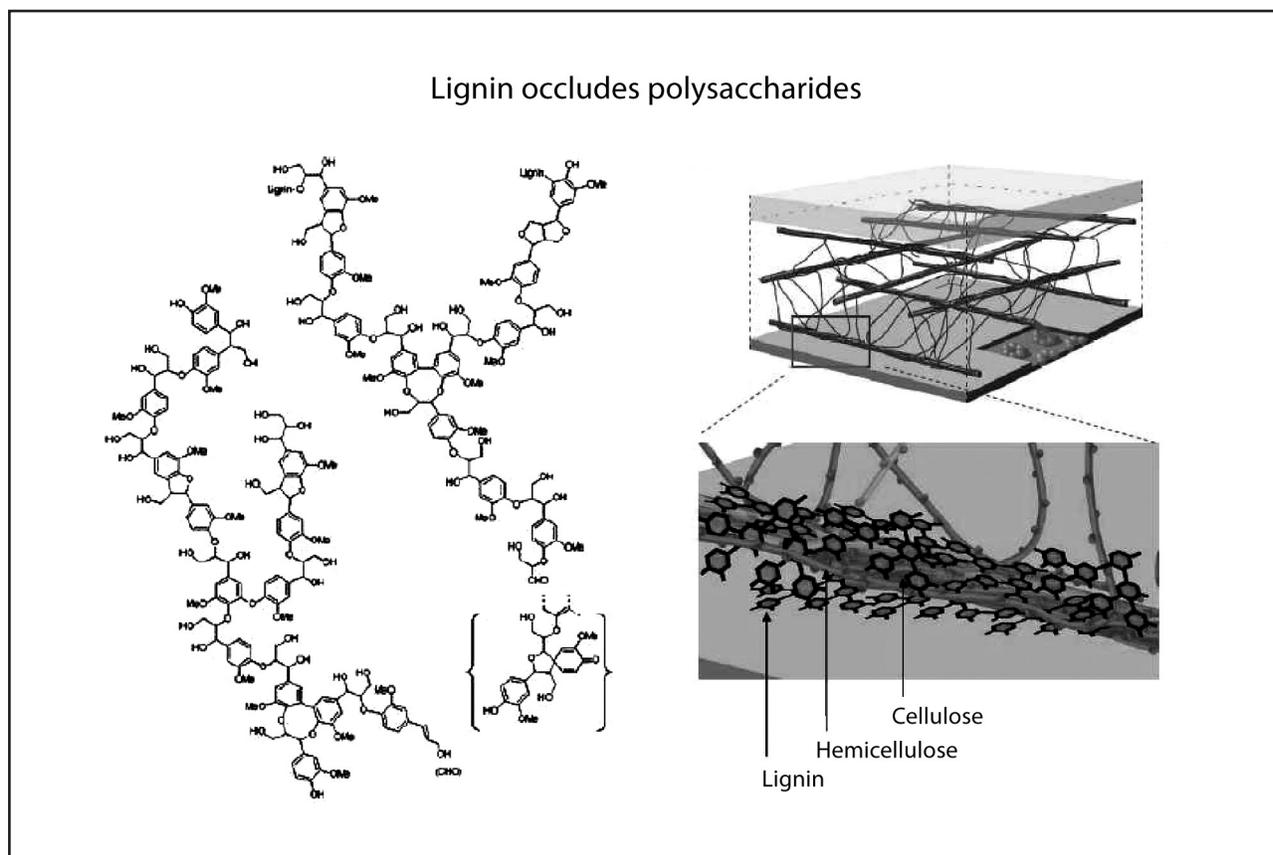


FIGURE 1 Polymer structure of lignocellulosic biomass.

TABLE 2 Chemical composition of different lignocellulosic resources (%)^{4,5,13}.

Resource	Cellulose	Hemicellulose	Lignin
Barley straw	40-44	28-30	20-22
Wood	44-50	20-26	17-30
Bagasse	50	20	30
Corn stover	36	23	17
Wheat straw	33	25	23
Rice straw	34	25	23

c) This hybrid route that enzymatically converts starch into fructose. An acid-catalyzed reaction converts the fructose into 5-hydroxymethylfurfural (HMF), which undergoes another catalytic reaction with hydrogen to yield the potential fuel 2,5-dimethylfuran (DMF).

Which is the best process? which one offers the greatest benefits? Etc. These questions are still unanswered especially with regard to economic feasibility.

In the following section lignocellulosic biomass conversion into its monomers will be discussed: cellulose will yield mainly glucose and hemicellu-

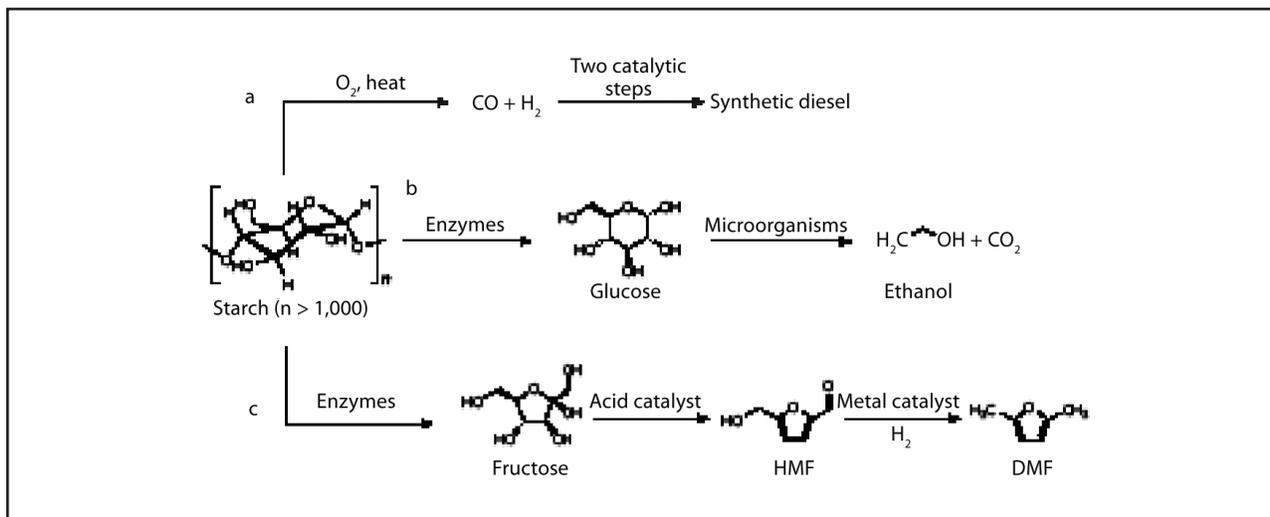


FIGURE 2 Conventional and Hybrid Biofuel Production Processes^{4,11}.

lose a mixture of sugars of 5 carbons (v. gr. xylose) and 6 carbons sugars (v. gr. fructose).

PRETREATMENT OF LIGNOCELLULOSIC BIOMASS

To achieve high yields of glucose, lignocellulose must first be pretreated, that is removed. The goal of pretreatment is to decrease the crystallinity of cellulose, increase biomass surface area, remove hemicellulose, and break the lignin seal, Figure 1. This pretreatment changes the biomass structure and improves downstream processing. Pretreatment methods include physical, chemical and thermal of some combination of the three. Pretreatment is one of the most expensive processing steps for the production of sugars from biomass, and the costs has been estimated to be as high as \$0.09 per liter of ethanol. Pretreatment is also one of the least understood processing options and recently several reviews have been published^{6,7,14,15}. According to Wyman *et al.*¹⁵, the following is a list of desirable pretreatment attributes:

1. Low cost of chemicals for pretreatment, neutralization, and subsequent conditioning.
2. Minimal waste production.
3. Limited size reduction because biomass milling is energy-intensive and expensive.
4. Fast reactions and/noncorrosive chemicals to minimize pretreatment reactor cost.

5. The concentration of hemicellulose sugars from pretreatment should be above 10% to keep fermentation reactor size and reasonable level and facilitate downstream recovery.
6. Pretreatment must promote high product yields in subsequent enzymatic hydrolysis or fermentation operations with minimal conditioning cost.
7. Hydrolysate conditioning in preparation for subsequent biological steps, should not form products that have processing or disposal challenges.
8. Low enzyme loading should be adequate to realize greater than 90% digestibility of pretreated cellulose in less than 5 days and preferably 3 days.
9. Pretreatment should facilitate recovery of lignin and other constituents for conversion to valuable co/products and to simplify downstream processing.

Physical pretreatment methods include ball milling, comminution (mechanical reduction of biomass particulate size) and compression milling. Solvents such as H₂O₂, ozone, glycerol, dioxane, phenol, or ethylene glycol have been used for biomass pretreatment, and these solvents are known to break apart cellulose structures and promote hydrolysis. However, solvent pretreatments appear

too expensive for practical purposes. According to MOSIER *et al.*, the most cost-effective and promising pretreatment methods are dilute acid, uncatalyzed steam explosion, pH controlled hot water, treatment with lime, and treatment with ammonia.

Table 3 shows the effect of various pretreatment methods on the chemical and physical structure of lignocellulosic biomass. Uncatalyzed steam explosion is used commercially to remove hemicellulose for the manufacture of fiberboard and other products by the Masomite process. High pressure steam is applied to wood chips for a few minutes without the addition of chemicals, and this process is terminated by decompression of the steam. This process increases the surface area without decrystallizing the cellulose and cellulose downstream is significantly improved.

Water treatments at elevated temperatures (200-230 °C) and pressures can increase the biomass surface area and remove hemicellulose. Three types of reactors are used for hot water pretreatment including co-current (biomass and water are heated together for a certain residence time), countercurrent (water and lignocellulose move in opposite directions), and flow through

(hot water passes over a stationary bed of lignocellulose). The advantage of hot water treatment is that acid addition and size reduction are not needed. A disadvantage of these methods is that hot water treatment forms sugar degradation products (furfural from pentoses and HMF from glucose). The degradation products can be minimized by controlling the pH of the hot water by addition of bases such as potassium hydroxide.

Dilute sulfuric acid treatments can be used to hydrolyze hemicellulose to sugars with high yields, change the structure of the lignin, and increase the cellulosic surface area. The disadvantage of this process is that not requires corrosive acid, with corresponding downstream neutralization, and special materials for reactor construction. Ammonia fiber/freeze explosion (Afex), where anhydrous ammonia is contacted with lignocellulose, can increase the surface area of the biomass, decrease crystallinity of cellulose dissolve part of the hemicellulose, and remove lignin. Treatment of the biomass with a less concentrated ammonia solution is known as ammonia recycled percolation (ARP). Ambient conditions can be used for lime treatments; however, the time required for these treatments is in terms of weeks. This process in-

TABLE 3 Effect of promising pretreatment methods on the structure and composition of lignocellulose biomass⁷.

Pretreatment method	Increases surface area	Decrystallizes cellulose	Removes hemicellulose	Removes lignin	Alters lignin structure
Uncatalyzed steam explosion	**		**		*
Liquid hot water	**	ND	**		*
pH controlled hot water	**	ND	**		ND
Flow-through liquid hot water	**	ND	**	*	*
Dilute acid	**		**		**
Flow-through acid	**		**	*	**
Ammonia fiber explosion (Afex)	**	**	*	**	**
Ammonia recycled percolation (ARP)	**	**	*	**	**
Lime	**	ND	*	**	**

* minor effect; ** major effect; n.d. = not determined.

volves mixing lime with water and spraying it onto the biomass. The mayor effect of lime pretreatment is removal of lignin. The biomass surface area is increased, and the acetyl and uronic acid fractions of hemicellulose are removed.

Table 4 shows the results of different pretreatment methods followed by enzymatic hydrolysis for production of sugars from corn stover. Table 5 lists the reaction conditions for the pretreatments. Using corn stover feed-stocks sugar yields of over 90% were obtained with the various pretreatments. A hot water treatment with a flow through

reactor was the pretreatment method with the highest overall soluble product yield; however, the xylose monomer yield was only 2.4% meaning this method did not produce xylose monomers. A dilute cid pretreatment method produced the highest amount of sugar monomers with a 92% yield. Results are expected to be different with other feedstocks.

An economic analysis of ethanol production using the various pretreatment methods shows that the cost increases as dilute acid < Afex < lime < ARP < hot water. The reason hot water

TABLE 4 Xylose and glucose yields of corn stover after various pretreatments followed by enzymatic hydrolysis¹⁴.

Pretreatments system	Xylose yields (% , max 37.7)			Glucose yields (% , max. 62.3)			Total sugar yields (%)		
	Stage 1	Stage 2	Total	Stage 1	Stage 2	Total	Stage 1	Stage 2	Total
Dilute acid	32.1(31.2)	3.3	35.3(34.5)	3.9	53.3	57.2	36.0(35.1)	56.6	92.5(91.7)
Flowthrough	36.3(1.7)	0.8(0.7)	37.1(2.4)	57.0	61.5(61.4)	40.8(6.1)	57.8(6.1)	57.8(57.7)	98.6(63.8)
Partial flow pretreatment	31.5(2.8)			4.3(4.2)					
Controlled pH	21.8(0.9)	8.9	30.7	3.5(0.2)	54.7	58.2	25.3(1.1)	63.6	88.9
Afex		ND (30.2)	ND (30.2)		61.8	61.8		ND/92.0	ND/92.0
ARP	17.8(0)	17.0	34.8(17.0)	0	59.4	59.4	17.8(0)	76.4	94.2(76.4)
Lime	9.2(0.3)	20.2	29.4(20.5)	1.0(0.3)	59.5	60.5(59.8)	10.2(0.2)	79.7	89.9(80.3)

Stage 1 is pretreatment of com stover and stage 2 is enzymatic hydrolysis after pretreatment with a cellulose loading of 60 EPU/g of glucan in the origina com stover. The value reported in each column is sugars plus oligomers, while the value in parentheses is the value for monomers only. A single value indicates that only monomers were observed.

TABLE 5 Optimal pretreatment conditions for ethanol production from corn stover¹⁵.

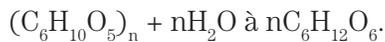
Pretreatment system	Chemicals	Temp (°C)	Pressure (atm)	Reaction time (min)	Solid conc (wt %)
Dilute acid	0.5-3.0 wt% sulfuric acid (0.49 wt%)	130-200(160)	3-15	2-30(20)	10-40(25)
Flowthrough	0.0-0.1 wt% sulfuric acid (0.0 wt%)	190-200(200)	20-24	12-24(24)	5-30
pH controlled	water or stillage	160-190(190)	6-14	10-30(15)	5-30(16)
AFEX	100% (1.1) anhydrous ammonia	70-90(90)	15-20	<5(5)	60-90(62.5)
ARP	10-15 wt% ammonia (15 wt%)	150-170(170)	9-17	10-20(10)	15-30
Lime	0.05-0.15 Ca (OH) ₂ /g _{biomass} (0.08)	25-60(55)	1	2-8 weeks (2 weeks)	10-20

The optimal reaction parameters are in parentheses.

pretreatment is so expensive is that it requires more enzymes to break down the xylose oligomers. If the oligomers could be successfully converted into ethanol (for other products), then the cost of making ethanol for the various pretreatment method decreases for the hot water, ARP, and lime methods, all of which make a significant amount of oligomers.

HYDROLYSIS OF LIGNOCELLULOSE

The hydrolysis reaction for cellulose conversion into sugar polymers is:



Hydrolysis of cellulose is significantly more difficult than for starches because cellulose is in a crystalline form with hydrogen bonding, Figure 3. The hydrolysis reaction can be catalyzed by acids or enzymes. Cellulose enzymes are able to catalyze the reaction with yields close to 100% at 50 °C. The National Renewable Energy Laboratory (NREL) of USA has estimated that the cost of unrefined sugar monomers, in an aqueous solution, produced

from lignocellulose would be 12-14 ¢/kg of sugar and others have projected the price of sugar could decrease as low as 5.3 ¢/kg.

Earlier cellulose hydrolysis kinetic models, developed by Saeman and others^{1,10,13}, involve two first-order reactions where the first involves cellulose hydrolysis to glucose followed by glucose decomposition. The accept model for acid hydrolysis, with diluted acid at high temperatures is shown in Figure 4.

Undesired byproducts including 5-hydroxymethylfurfural (HMF) and levulinic acid are produced by acid-catalyzed degradation of sugars. Most hydrolysis data were fit to his sample model from 1945 to 1990, and Table 6 shows the model parameters from various studies. Using these parameters the maximum yield of glucose is always less than 70%. Enzymatic hydrolysis can produce glucose yield above 95% as shown in Table 4. The acid hydrolysis of cellulose has a lower activation energy than lignocellulose, thus showing the effect of ligning on the acid hydrolysis reaction.

More complicated kinetics models have been developed based on mechanistic data. Oligomer

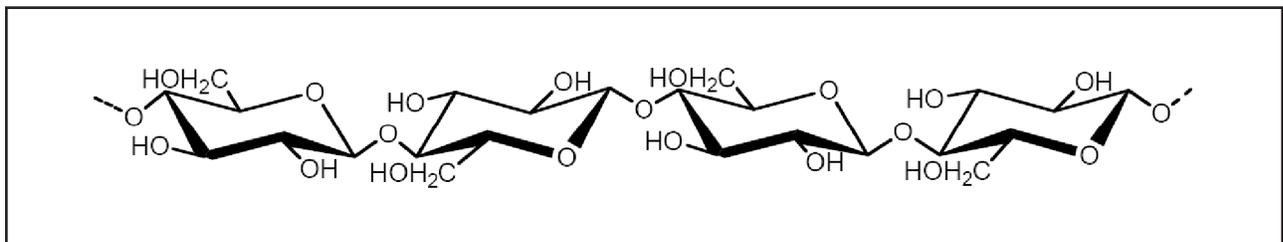


FIGURE 3 Chemical structure of cellulose (crystalline polymer of glucose connected via beta linkages)¹.

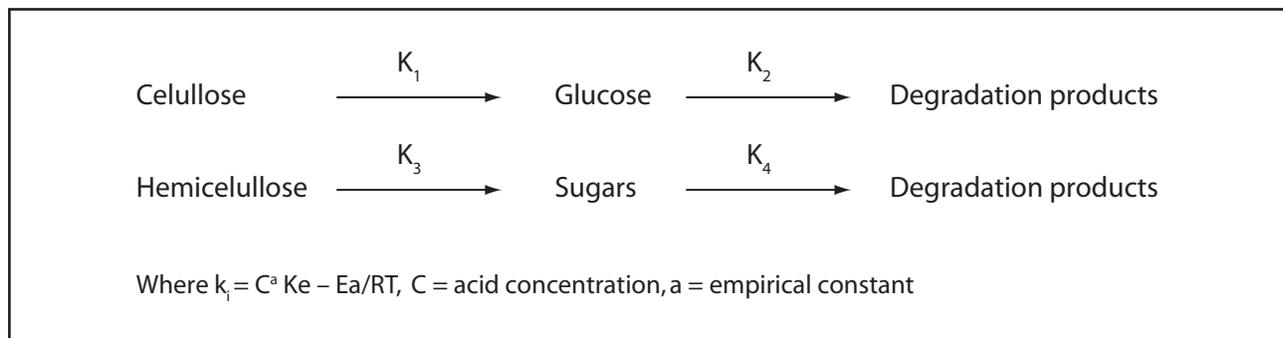


FIGURE 4 Model of acid hydrolysis at high temperature^{10,13}.

TABLE 6 Kinetic parameters for acid hydrolysis of various biomass feedstocks with the Saeman Model^{1,10}.

Feed	Temp (°C)	Acid conc (wt %)	K_1 (min ⁻¹)	K_2 (min ⁻¹)	E_1 (kJ/mol)	E_2 (kJ/mol)	m	n
Glucose	160-260	?		1.85×10^{14}		136		1.0
Cellulose	100-130	5-40 H ₂ SO ₄	1.57×10^{14}		142		1.42	
Douglas fir	170-190	0.4-1.0 H ₂ SO ₄	1.73×10^{19}	2.38×10^{14}	180	137	1.34	1.02
Kraft paper	180-230	0.2-1.0 H ₂ SO ₄	28×10^{19}	4.9×10^{14}	189	137	1.78	0.55
Newsprint	200-240	1.0 H ₂ SO ₄	28×10^{19}	4.8×10^{14}	189	137	NR	NR
Solka-floc	180-240	?	1.22×10^{19}	3.79×10^4	178	137	NR	NR
Cane bagasse	100-130	5-40 H ₂ SO ₄	1.15×10^{21}		152		1.42	

Saeman model is represented as cellulose + water $\xrightarrow{k_1}$ glucose $\xrightarrow{k_2}$ degradation products where $k_1 = K_1 (\text{Con}_{\text{acid}})^m \exp(-E_1/RT)$ and $k_2 = K_2 (\text{Con}_{\text{acid}})^m \exp(-E_2/RT)$ (with Con_{acid} in wt fraction of acid).

conversion into glucose is 2-3 times faster than conversion of cellulose to glucose; however, oligomers have been observed during hydrolysis. These observations lead to the development of a two-step model where cellulose is converted into oligomers, which are then converted into glucose. Others have observed⁸ that in addition to the hydrolysis pathway another pathway occurs that produces a modified cellulose that cannot be hydrolyzed to glucose. Importantly, this model suggests that cellulose structural rearrangements can occur with high-temperature treatments. The acid-hydrolysis reactions are heterogeneous with the solid biomass reacting with liquid acid. Thus, mass transfer limitations also can play a role in hydrolysis.

The mechanism for C-O-C bond cleavage in cellulose involves protonation of glucosides bonds. The proton can either attack the oxygen bond between the two glucose units of the cyclic oxygen, which define two different pathways. The mechanism is thought to involve the rapid formation of an intermediate complex with the oxygen and proton, followed by the slow splitting of glucosidic bonds by the addition of a water molecule.

Heterogeneous reactions occur during cellulose hydrolysis in the biomass where the acid first penetrates into disordered cellulose regions leading to an initial rapid decrease in the degree of polymerization (DP). After the rapid initial decrease, the DP reaches an asymptotic value

where the DP remains at a constant value called the degree of polymerization (LOPD). The LOPD is dependent on the type of cellulose samples and is reached when only 2-5% of the sample has been hydrolyzed. The average length of crystallite in the cellulose sample is considered to be the same as the LOPD. Oxidation of cellulose (with oxidizing agents such as H₂O₂, NaClO₂, O₃, KBrO₃ etc.) prior the hydrolysis or during progressive hydrolysis reduces the DP of partially hydrolyzed residues. This treatment decreases the aldehyde concentration and increases the carboxylaldehyde concentration, which prevents recrystallization. Recrystallization can occur during acid or enzymatic hydrolysis.

Prior the enzymatic hydrolysis, the cellulose structure must be pretreated to open up the structure of biomass for reaction of the cellulose with cellulase. Initially, a process was designed to produce ethanol through enzymatic hydrolysis by separate hydrolysis and fermentation (SHF) steps. This involved using improved enzymes from the fungus *Trichoderma reesei*. Problems with these methods are that cellubiose and glucose inhibit the reaction, which increased enzyme cost. This problem can be reduced by a process known as simultaneous saccharification and fermentation (SSF) where the vessel contains both cellulose and fermentative organisms to convert glucose rapidly to ethanol. This process significantly reduces the concentration of glucose. Although the tempera-

ture of the SSF process is lower than the optimal temperature for enzymatic hydrolysis because the fermentation organisms are not stable and these higher temperatures, the rates, concentrations, and yields are still better than for SHF.

Cellulases, the enzymes that catalyze cellulose hydrolysis, were initially categorized based on the reaction they catalyze. More recently, they have been classified based on structural properties⁵. Three major types of enzymatic reactions are reported including (1) endoglucanases or 1-4- β -D-glucan glucanohydrolases, (2) exoglucanases or 1-4- β -D-glucan glucanohydrolases (also known as celloextrinases) and (3) β -glucosidases or β glucoside glucohydrolases. Endoglucanases react with internal amorphous cellulose sites to produce shorter chains of varying lengths and expose chain ends. Exoglucanases hydrolyze the ends of cellulose produced by endoglucanase in a progressive manner to produce cellobiose as the major product. β -glucosidases convert cellodextrins and cellobiose to glucose. The hydrolysis mechanism in an enzyme occurs using a proton donor and nucleophile or base. Cellulase systems

act in a coordinated manner to efficiently hydrolyze cellulose and consist of more than just a combination of the three enzymes systems. Recent reviews have been published on kinetic modeling of cellulose enzymatic hydrolysis.

There are only two companies in the world that today produce commercially cellulases, Genencor in USA and Novozymes in Europe. Last September, Genencor introduced a new enzymatic preparation known as Accelerase1000 which has 4 different enzymatic activities. Figure 5 presents the results of using such enzyme on washed acid-pretreated corn stover and sugarcane bagasse; it is interesting to observe that a yield of almost 90% was achieved for cellulose digestibility.

Even that hemicellulose offers an important amount of fermentable sugars, its enzymatic hydrolysis is more complicated than the one of cellulose. This polymer is composed of a mixture of sugars of 5 and 6 carbons which required several different enzymes to break it⁵. In Figure 6 the main glycoside hydrolase and carbohydrate esterase enzyme families for degrading hemicellulose are shown: endoxylanase, beta-xylosidase,

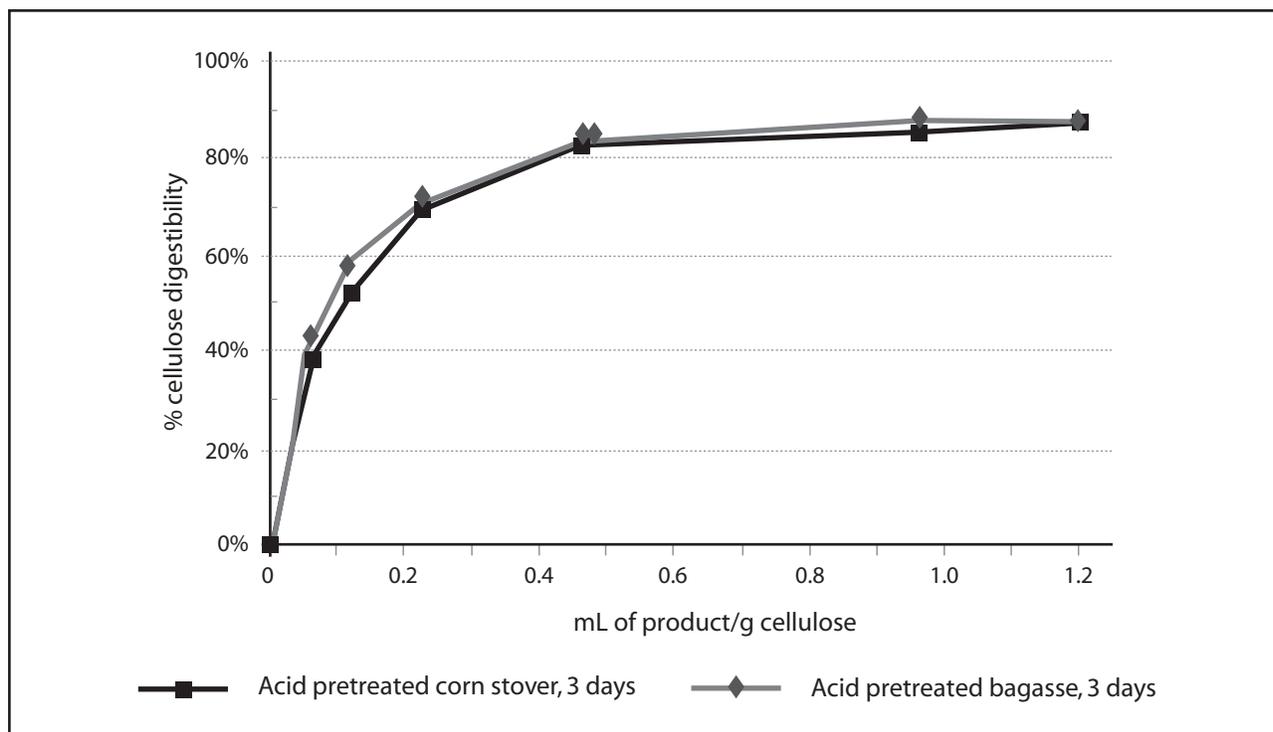


FIGURE 5 % Cellulose digestibility vs mL of product per g cellulose for washed acid-pretreated corn stover and sugarcane bagasse using Accelerase™ at 7% cellulose loading, 50 °C, pH 5.0, and in 3 days³.

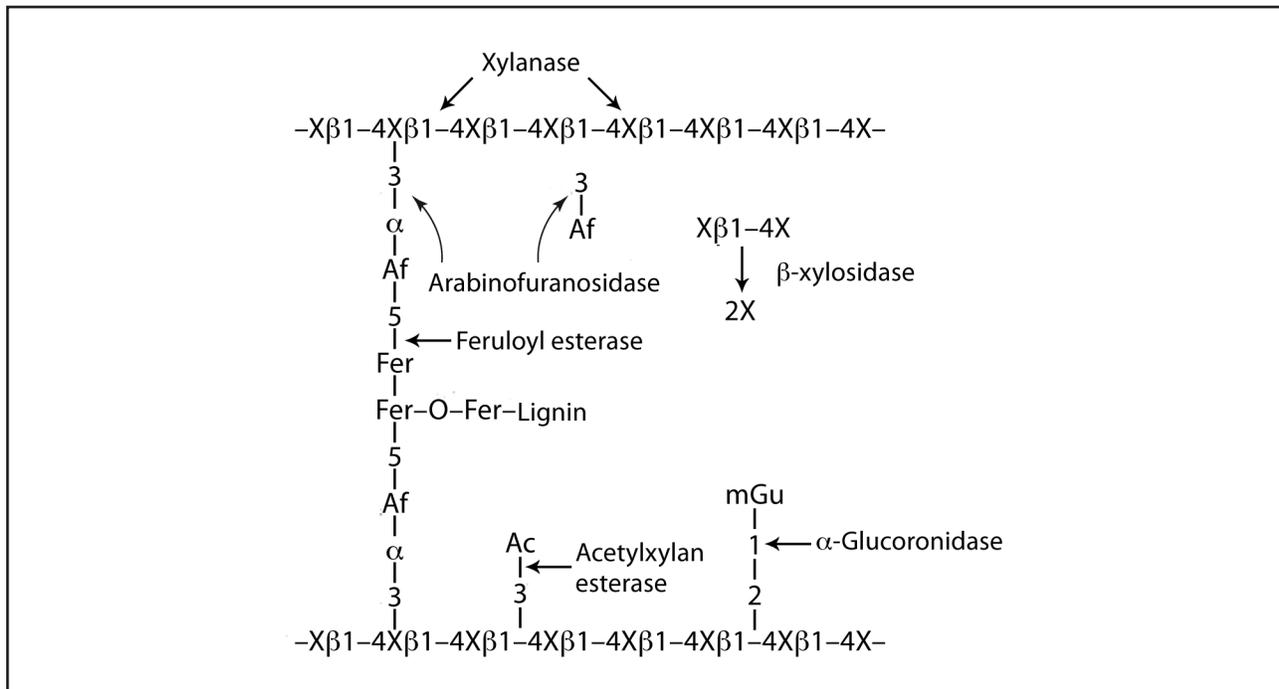


FIGURE 6 Different enzymes require for hydrolysis of hemicellulose⁵.

alpha-Larabinofuranosidase, alpha-glucuronidase, alpha-galactosidase, acetylxylan esterase and feruloyl-esterase. These requirements make difficult and expensive the enzymatic hydrolysis of hemicellulose.

Acid hydrolysis of hemicellulose occurs under less harsh conditions than cellulose because hemicellulose is an amorphous polymer. Hemicellulose hydrolysis even occurs in hot water (~ 210 °C), where the water is thought to break down hemicellulose and release acetic acid, which continues to catalyze the reaction. Water-soluble oligomers from in high yields with hot water treatments. Dilute acid treatment of lignocellulose at 160 °C, 10 min reaction time, and 0.7 wt% acid, yields 85-90% of the hemicellulose sugars. Kinetic models usually incorporate two types of hemicellulose a fast hydrolyzing type and a slow hydrolyzing type. The proportion of fast and slow fractions is typically 65 and 35% as determined by fitting kinetic data. Oligomer intermediates are experimentally observed but frequently ignored in kinetic models. Although significant effort has been devoted to describing the kinetics of hemicellulose hydrolysis, the models do not predict consistent results. For

example, the rate of xylose degradation in kinetics models is different than the rate of pure xylose degradation. The hemicellulose also is associated with lignin, and this type of bonding could change the kinetics. Future mechanistic work could help clarify the heterogeneous mechanisms of acid hydrolysis of biomass leading to further process improvement.

Some research groups are focusing their efforts into the design and development of new catalytic systems for cellulose hydrolysis. An interesting approach published recently¹² takes into account the knowledge of enzyme structure and function and while still been based on acid catalysis uses the dicarboxylic maleic acid, in this case the difunctional nature of the acid enables it to have hydrolytic activity while at the same time minimizes the degradation of the monosaccharides that are formed.

ECONOMICS OF LIGNOCELLULOSE CONVERSION PROCESSES

Numerous studies have discussed the economics of biomass conversion processes over the last 20-30 years. Some these studies have been

revisited and compiled using a single base and a single set of assumptions. For this purpose, the manufacturing costs have been split into two major contributions, namely the feed and the processing costs. The former covers the cost of purchasing the feedstock. The latter covers the cost of installing and running the manufacturing plants, v. gr. the cost of plant, the labour as well as the energy and chemical consumed. The economics of the various technologies can then be visualized by plotting the processing cost against the feed of the various process alternatives, as done in Figure 7. The diagonal “eco-cost” lines represent overall manufacturing cost.

Figure 7 displays processes that produce transportation fuels from bio and fossil feedstock, v. gr. from lignocellulose, starch and vegetable oil as well as from crude oil and natural gas. It shows that the cost of oil refining is dominated by feed cost whereas the costs of gas conversion (v. gr. *meOH* or Fischer-Tropsch synthesis) are dominated by technology. Similarly, biofuels derived from vegetable oils are dictated by feed cost whereas those derived from lignocellulose are dominated by technology. The economics of biofuels derived from starch and sugars is intermediate to these two

extremes. There is obviously a trade-off between feedstock cost and plant cost. Feedstocks, such as vegetable oil, may be expensive (\$ 13-18/GJ or \$ 500-700/ton) but they are easy to convert. Others like lignocellulose may be cheap (\$ 2-4/GJ or \$ 34-7/ton dry) but are very difficult to convert.

The diagonal lines also indicate that production of biofuels typically cost \$ 15-25/GJ, which exceeds the \$ 5-15/GJ of fossil fuels. Biofuels appear to be competitive with oil refining only at high oil prices, between \$ 50-75/barrel.

Despite the high processing costs, the cost of the biomass conversion plants reported in the literature appeared to follow the same general laws as those of chemical and fuel plants. Irrespective of the technology applied, the plant cost of biofuel plants correlates with the overall energy loss of the plant exactly as do other chemical and fuel plants. It is then not surprising to see the cost of biomass conversion plant decreasing with increasing energy efficiency, after recalculation to a single plant size of 400 MW intake (v. gr. 680 kt/a lignocellulose), Figure 8.

Based on the analysis presented above, it is imperative to reduce the processing cost of lignocellulosic feedstock. Improvements could be

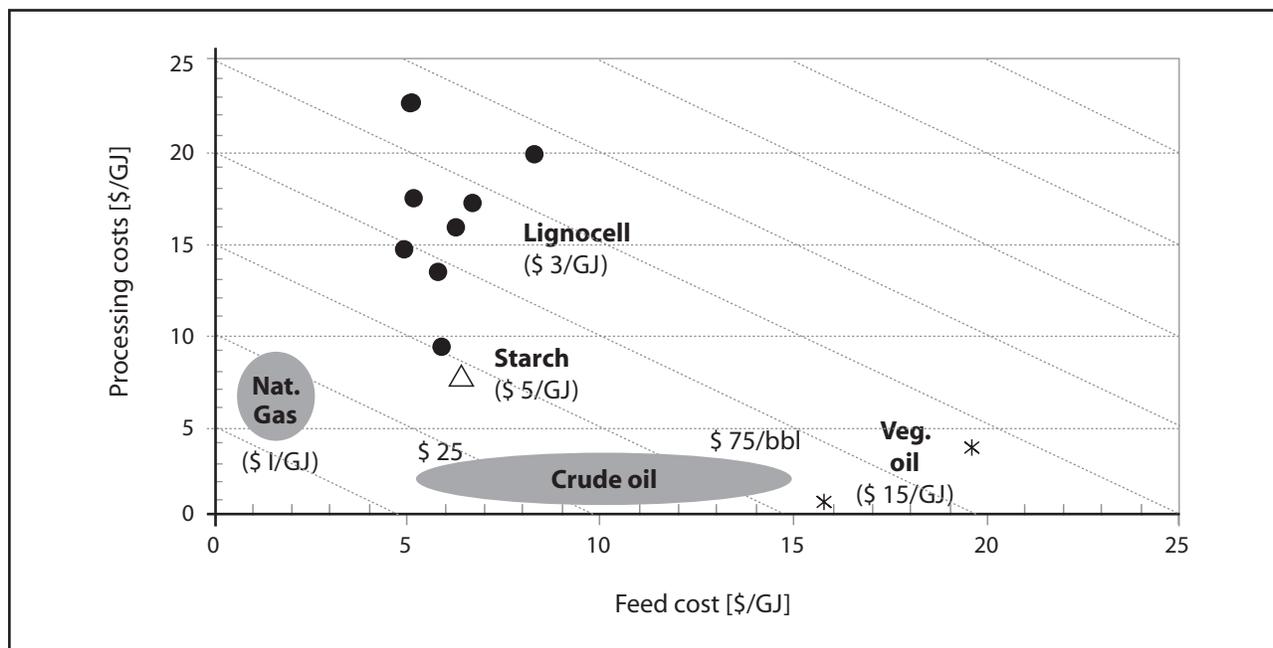


FIGURE 7 Feed and processing cost of transportation fuels derived from lignocellulose and fossil resources (the biofuel plants are set at 400 MW intake, which corresponds to 680 kt/a of lignocellulose)⁶.

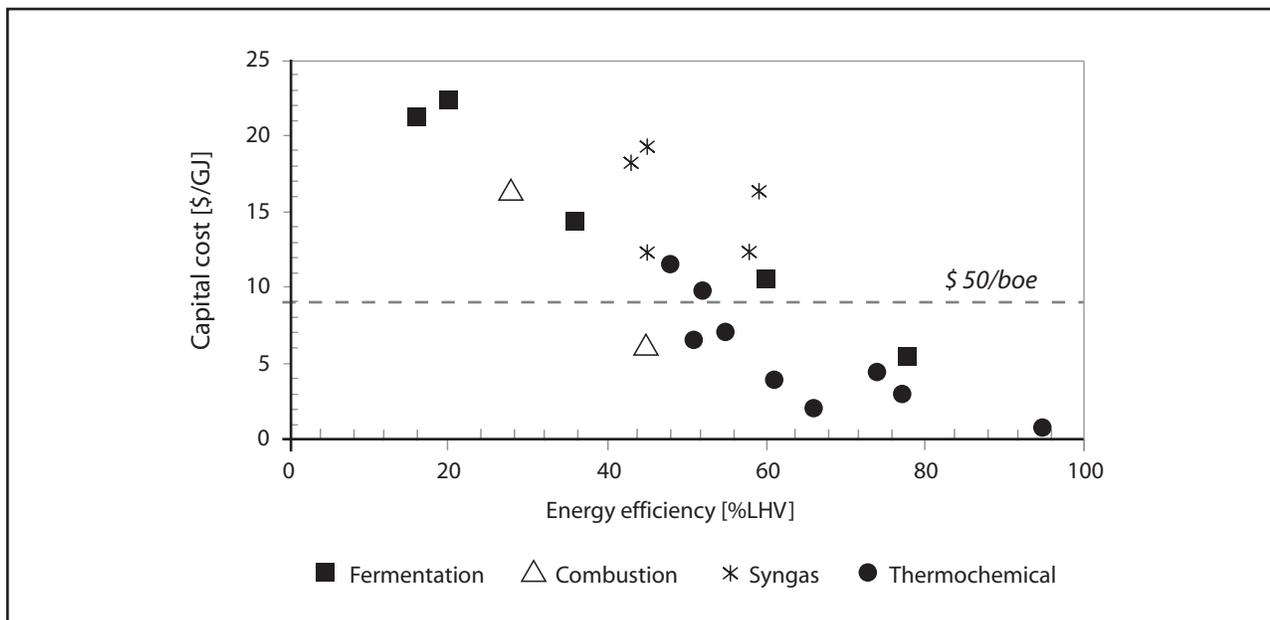


FIGURE 8 Capital cost of biomass conversion plants (400 MW intake, 25% capital charge, \$2005)⁶.

sought in the overall energy demand of the plant. One could, for instance, look at the handling and pretreatment of solid feedstock, which require heavy and energy-consuming equipments. The purification of the product can also be energy- and capital-intensive. For instance, hydrolysis and fermentation technologies often result in a product that is highly diluted in water and requires expensive recovery by distillation or extraction.

Equally important is to increase the scale of the process as much as possible. The contribution of the plant cost to the overall manufacturing cost is known to decrease by 2025% for a two-fold increase in plant size⁶. However, the scale of biofuel plants might not be limited by technology but rather by the amount of feedstock that can be collected within a reasonable radius and transported to the plant at reasonable cost. In fact the intake of 400 MW (or 680 kt/a of lignocellulose) assumed here requires a fairly large collection area of some 6,000 km².

The analysis here was limited to the manufacture of finished biofuels. The economics of converting the biomass to biocrude, electricity or chemicals was omitted for the sake of simplicity but is discussed elsewhere. Accordingly, biocrude may compete with fuel oil at an oil price of \$ 50-80/barrel, biofuel may compete with gasoline and

diesel at \$ 70-110/barrel, and green-electricity is affordable at \$ 80-100/barrel oil.

Even in USA the advocates of cellulosic ethanol put the capital costs of constructing a manufacturing plant at more than twice those for a corn-based facility, and other estimates range from three times the cost to five⁹. Many researchers believe that the most promising way to make cellulosic biofuels economically competitive involves the creation-of the discovery-of “superbugs”, microorganisms that can break down cellulose to sugars and then ferment those sugars into ethanol. The idea is to take what is now a multistep process requiring the addition of costly enzymes and turn it into a simple, one-step process, referred to in the industry as consolidated bioprocessing.

But if cellulosic biofuels are to be replacing gasoline within five to ten years, facilities will need to start construction soon. This fall, Range Fuels, a company based in Broomfield, Colorado, announced that it had begun work in Georgia on what it claims will be the first commercial-scale cellulosic-ethanol plant. The Range facility, which will use thermochemical technology to make ethanol from wood chips, is scheduled to reach a capacity of 20 million gallons in 2008 and eventually increases to 100 million gallons a year. Meanwhile

other company, Mascoma has announced several demonstration units, including one facility in Tennessee that will be the first cellulosic-ethanol plant built to use switchgrass. But these production plants are federally subsidized or are a result of partnerships with state development organizations which makes difficult and risky the economic evaluation of such projects, they are still in the phase of demonstration.

Being one of the most important limitations for the hydrolysis of lignocellulose, the price of cellulase. Several companies and research groups have directed their efforts into finding new ways, less expensive, to produce the enzyme. One of these studies carryout an economic analysis evaluating two different methods for production of cellulase; the traditional submerged fermentation (SmF) and the new solid state cultivation (SSC). As it can be seen in Table 7, the SSC method requires less investment and has lower cost of production, \$ 15.67/Kg of cellulase vs \$ 40.36 using SmF method. In the market the price is \$ 90/Kg.

RECOMMENDATIONS FOR FUTURE RESEARCH

In the document of the State of São Paulo Research Foundation², are described many research projects which are currently being developed in

TABLE 7 Economic analysis of cellulase production methods for bioethanol (data in million of dollars)¹⁶.

	SmF	SSC
Investment		
– Main equipment	4,898	3,562
– Direct fixed capital	28,627	22,021
Annual cost		
– Raw materials	3,753	0.458
– Utilities	16,907	0.164
– Operarion costs	30,576	8.230
Cellulase cost (dollars per Kg)	40.36	15.67

SmF: Submerged fermentation
SSC: Solid state cultivation

Brazil concerning new technologies for the use of sugarcane bagasse and its conversion into ethanol.

As a conclusion of this review, Table 8 was constructed to summarize the main problems to be solved in the processing of lignocellulosic biomass to obtain bioethanol:

- The design of the process has been done by stages and carried out in a linear way. This scope has permitted a limited advance in the last 30 years or so. It is recommended that a more holistic view should be tried in the development of new bioprocesses.
- The process involved several stages, each stage has a yield lower than one and the total yield then is lower than 50%. The lower yields are usually in the pretreatment and in the hydrolysis steps.
- The total cost of producing ethanol from lignocellulosic materials is obtained adding the costs of each stage and the cost of the lignocellulose source and of the enzymes required are the more important ones.
- The idea will be to increase yield, reduce costs (decrease the number of the stages) and in that way the cost of production of ethanol will diminish.

For a research strategy in the area of hydrolysis of lignocellulose, I will answer the following questions:

1. Is Brazil doing the right research?

According to the document of Fapesp² the projects at laboratory and pilot plant that are being carried out have focused the problem on the right track. In the short term most probably acid hydrolysis of lignocellulosic materials will be the method to use, and in that sense the Dedini Rapid Hydrolysis Process seems to be a very important initiative. Also it is recommended that at least 2 or 3 projects are financed in the area of celluloses: looking for new strains for production, searching for new enzymatic activities and more important one, the preparation of a cocktail of enzymes and the testing of them with real raw materials. In this regard it has to be

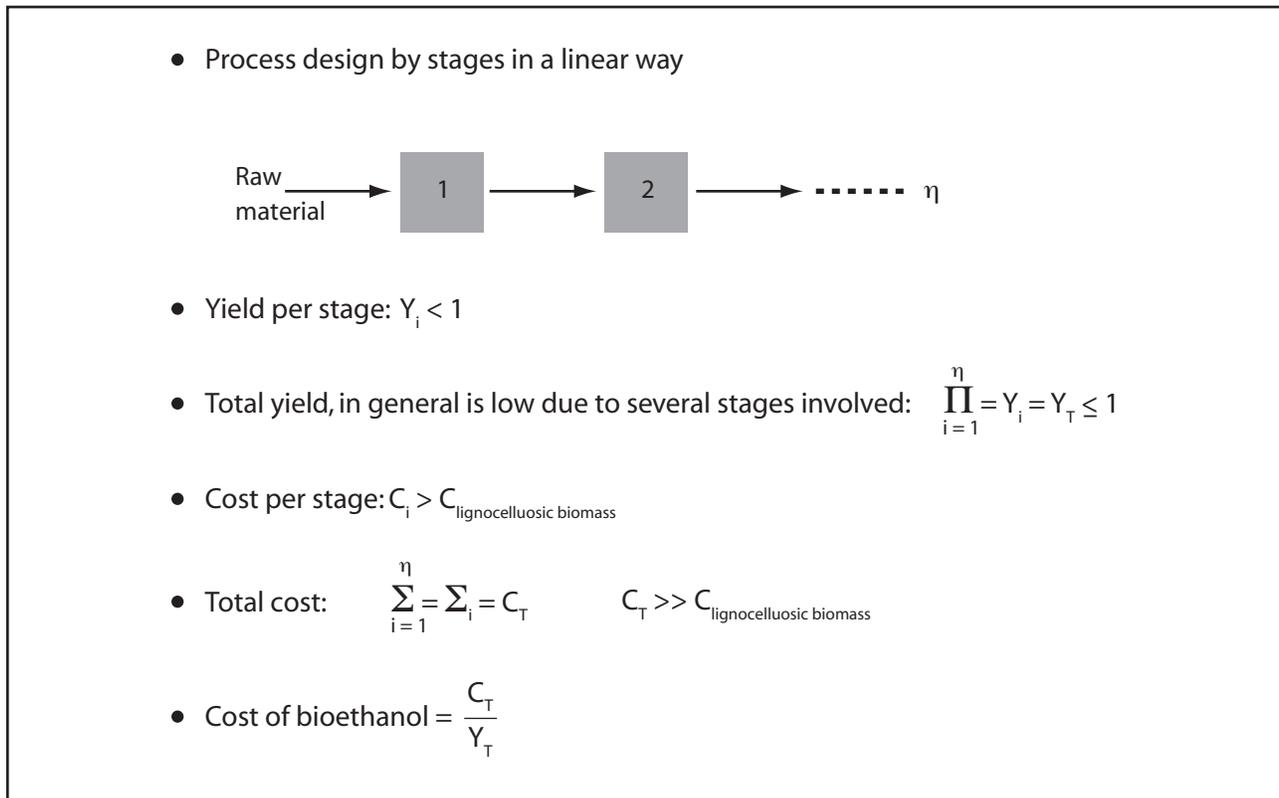


FIGURE 9 Main Problems in the Processing of Lignocellulosic Biomass to Obtain Bioethanol.

taken into account that Novozymes has a production facility in Brazil and most probably they were produce cellulases if the market needs them.

2. Are there human capacities to overcome the difficulties?

During my stay to São Paulo I visited two universities, Unicamp and Lorena, in both places I found a research group with the strong experience and clear ideas of what to do next. The Fapesp document indicates that in Rio de Janeiro there are other strong and large groups working on biotransformation of lignocellulose into ethanol. One missing element is the economic analysis of the projects and the developed production processes. I strongly recommend the construction or buying an economic simulator in order to do frequently economic evaluations.

3. Is industry university partnership important?

Hydrolysis of lignocellulose has been a research area for more than 63 years and

the results have been limited and in some cases useless. I believe that the partnership between university and industry is a must in this field. The new processes will required development of new equipment, for example for acid hydrolysis at high temperatures the reactor must be very well design and constructed with the right materials, also the problems of the scale-up will be present all the time in this field, so there must be pilot plant facilities at least.

4. Is international cooperation important and possible?

Brazil is a world leader in ethanol production, together with USA; both countries are trying to develop new technologies to use lignocellulosic materials. One way in which Brazil could advance more rapidly is through international collaboration, for example if there are research groups in Mexico or Chile or in Europe or Canada, they should be contacted and the establishment of joint

collaborative programs should be promoted and financed. In the process of lignocellulose to ethanol, today the bottleneck are in the pretreatment and hydrolysis stages, the rest of the process is quite well known and mastered by researchers and companies in Brazil. One area which has not been developed yet, is what will be the real yields using real raw material in large scale. The six plants that USA has set up for production of ethanol based on lignocellulose and using different technologies will be on stream in a few months and it will be interesting for Brazil to follow up the results.

5. **What is the future of the different hydrolysis technologies?**

No one knows for sure, of the six demonstration plants in USA, three of them use enzymatic hydrolysis and the others chemical technologies. Also all of them are based on different raw materials in order to find out what are the difficulties in large scale production. The price of oil will be

an important factor to determine which technology will be the winner and again it comes to mind the need for an economic simulator to study different technologies but also options for production scenarios. The topic of production of enzymes is also a present concern because today only two companies can produce cellulases at commercial scale, most probably there will be other enzyme producers in the world.

6. **Will hydrolysis technologies ever become competitive?**

Again the answer it is still in the air. All the theoretical evaluations about hydrolysis of lignocellulose indicate that the potential for ethanol production is very large but at the same time today the cost of production is only competitive when the barrel of oil is very high. Also as it has been mentioned several times in this paper, the real problems or large scale have not been solved and is even less known what will be the economic impact of them.

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