

Low-cost, concentrated sugar production from lignocellulosic feedstocks

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ABSTRACT

In the last few years, sugar is emerged as the main feedstock to derive several potential biofuels and chemicals. The cost availability of these fuels/chemicals are vastly depends on the source of sugar. Currently most of the processes are based on sugar from corn, sugar cane and sheet beets, etc. use of such food-derived raw materials is not sustainable. Lignocellulosic sugar is sustainable however is not economical compared to other food-based feedstocks. We are developing technologies to produce low-cost sugar from lignocellulosic biomass feedstocks which are not part of nation's food supply and are readily available. Based on the pilot results, we hypothesize that sugar cost should be less than 25 cents/lb which will make it competitive with the 1st generation food based sugars.

Keywords: lignocellulosic feedstock, sugar, biofuel

1 INTRODUCTION

Biofuels produced from biomass such as forestry waste and organic waste from commercial plants such as paper mill could help to reduce both the world's dependence on oil and CO₂ production. With the worldwide availability of lignocellulosic biomass, there has been a great deal of interest in utilizing them for the production of bio fuels or valuable chemicals.

The bioconversion of lignocellulosic materials to fuels and chemicals is composed of three major steps; pretreatment (fractionation), enzymatic hydrolysis and fermentation. Pretreatment is usually done to remove lignin (possibly in a useful form) and increase accessibility of the cellulose to hydrolytic enzymes. The pretreatment and hydrolysis have been identified as one of the major economic barriers toward commercialization of lignocellulosic conversion.

The fractionation is done by a process known as pulping. Chemical wood pulping involves the extraction of cellulose from wood by dissolving the lignin that binds the cellulose fibers together. The processes principally used in chemical pulping are kraft, sulfite, neutral sulfite semichemical (NSSC), and soda.

The kraft process alone accounts for over 80 percent of the chemical pulp produced in the United States and is the dominant chemical pulping process, but it has a major shortcomings, the resultant pulp is too expensive for any possible sugar production. The shortcoming in kraft pulping

has led to the development of several organosolv fractionations of the wood constituents.

The organosolv pulping also has problems associated with chemical recovery of solvent. Economics of fractionation and sugar extraction, which are based only on cellulose, are not attractive and it is of vital importance to maximize the efficiency of the pulping process by recovering the by-products (lignin and hemicelluloses), which represent about 50wt% of the dry wood. In this context, we developed an organosolv processes, based on the use of organic solvents as delignification agents, in which it is possible to break up the lignocellulosic biomass to obtain cellulose fibers, high quality hemicelluloses and lignin.

This paper describes a next generation biorefinery concept (Figure 1) where all the components of biomass feedstock are converted to valuable biofuels and chemicals [1]. From lab scale to pilot scale transformation is also described here. There are three major steps to achieve this next generation biorefinery concept: 1) 2nd generation organosolv process to fractionate biomass [2], 2) in-situ value added chemicals during the fractionation process [3] and 3) low cost sugar production from the cellulosic fraction [1]. The advantage of the 2nd generation organosolv process is that all the fractions are collected separately and utilized separately to make this process more selective and profitable.

2. BIOREFINERY PILOT PLANT DEMONSTRATION

21st century is looking biorefinery technologies which not only produce biofuel which can fit to current transportation infrastructure but also produce simultaneously valuable chemicals from the biomass feedstocks [4]. Strategic utilization of byproducts from a biofuel process will make the process more economical to compete with the petrochemical industry [1] [5]. During the last 6 years, AST has adopted an organosolv process technology idea presented by the University of Wisconsin Stevens Point to design its integrated bio-refinery (Figure 1). To prove the capabilities, AST has developed and built its integrated bio-refinery pilot production plant that has been in service since 2009.

AST's integrated pilot bio-refinery includes a 20 Kg batch digestion system that can fractionate woody biomass in 30 min at the reaction temperature, which is lower than the 1st generation ethanol Organosolv process. The output of the

digestion system includes cellulose, hemicelluloses, and lignin [6]. Depend on the applied pressure and temperature the hemicelluloses can be converted to C5 sugar, furfural or other high value chemicals [7].

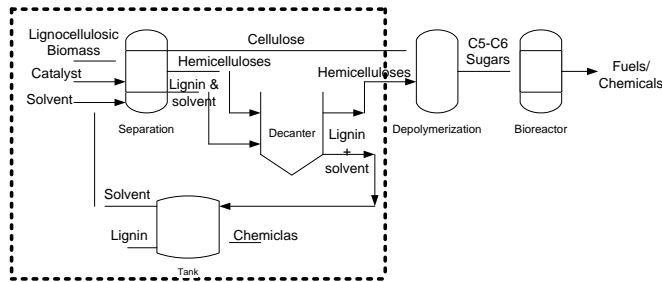


Figure 1. Process Flow Diagram of our next generation biorefinery.

AST digestion system (Figure 2) is a fully controlled pressure cooker that can hold up to 350 PSI at 300 Fahrenheit. This system is being used mainly to remove lignin from the biomass and produce proper cellulose for sugar production [8].



Figure 2, AST's Digestion System

After the digestion process is completed, the resultant output is a liquid phase (mixture of aqueous and organic layers) and a solid phase (cellulose and remaining lignin). The liquid phase is drained into a settling tank where the aqueous layer separates itself from organic layer (Figure 3).

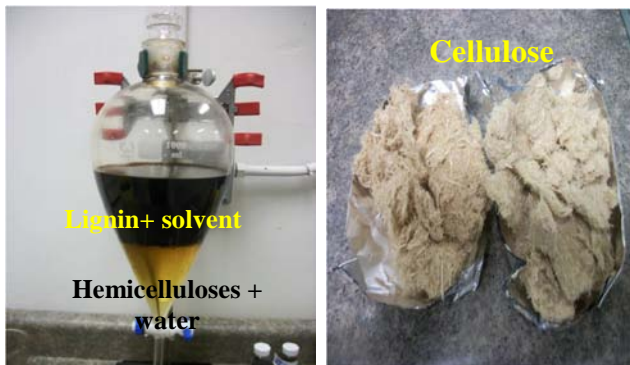


Figure 3, Aqueous / Organic layers, and Cellulose

Once components are separated, we use our 100 L hydrolysis unit to convert the oligomers to monomer sugars (Figure 4). Based on the pilot results, we hypothesize that sugar cost should be less than 25 cents/lb which will make it competitive with the 1st generation food based sugars.

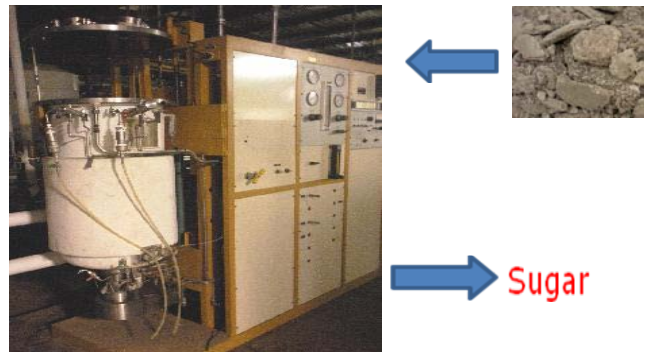


Figure 4, AST Hydrolysis Unit

The monomeric sugars produced are being converted to various alcohols (ethanol, butanol, isobutanol) and high value chemicals (isoprene, lactic acid, 5-(chloromethyl) furfural) in our 150L pilot scale fermenter (Figure 5) [9] [10].

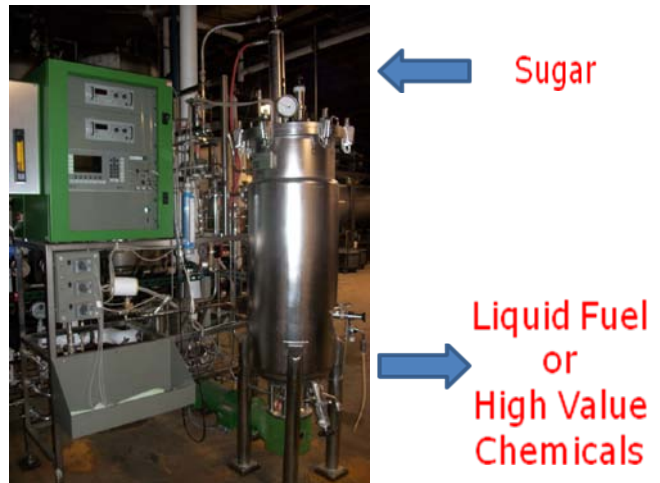


Figure 5, AST's pilot fermenter

AST also has developed a proprietary process to produce concentrated sugar syrup from lignocellulosic biomass feedstocks. This process reduces the production cost of sugar syrup, reduces the use of external energy, and reduces the amount of water and expensive distillation setup. In addition, AST in collaboration with UWSP has developed processes that can use the feedstock comes from paper mill and logging waste, which if they are processed efficiently, can produce great profit.

The liquid phase after settling will be separated into aqueous and organic layers. The aqueous layer includes

some solvent, some C5 sugar that usually being recycled for the next batch of digestions process. The organic layer that included solvent and valuable lignin, depends on market demand can go through chemical precipitation or flash evaporation separation processes [11]. The lignin produced from this fractionation process can also be used in one of our two pilot fast pyrolysis units to produce bio-oil and hydrocarbon fuels through a catalytic process.

3. EXPERIMENTAL

AST's integrated biorefinery process summarizing butanol organosolv pretreatment, separation and purification stages as well as solvents (solvent and water) recovery units is shown in Figure 6. Lignocellulosic raw material will be treated by liquid solvent, in a pilot scale 20 kg batch reactor at a controlled temperature and pressure. Experimental conditions that has been the most favorite are: solvent to water ratio of almost 50/50 m/m; temperature depend on the type of biomass between 160 to 180 °C; reaction time about 30 min at temperature; and liquid to solid ratio of about 5:1. After fractionation, the liquid are collected to a separate container where the lignin-liquor and hemicelluloses are separated. The cellulose (solid) are centrifuged to collect the remaining solvents in the fiber; washed with water and process for enzymatic hydrolysis. The average cellulose yield is generally 40-45 wt%.

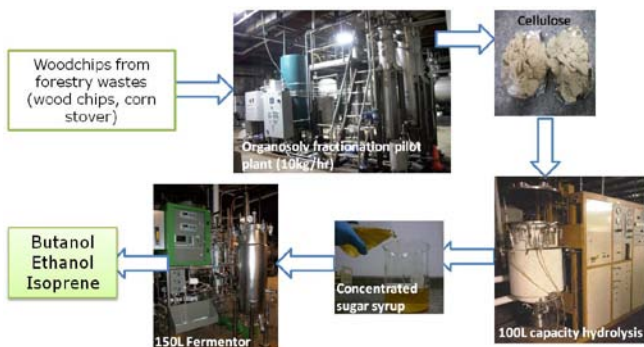


Figure 6: AST's pilot plant demonstration facility to produce low-cost concentrated sugar from lignocellulosic feedstocks.

The solvent (and other chemicals like furfural and esters, Figure 7) from the liquor are distilled off to produce high quality lignin. In this process 95% lignin is recovered from the biomass. This lignin is of high purity with melting properties around 178 °C and soluble in wide range of organic solvents. These properties make this lignin a strong candidate to replace petrochemical based feedstocks to produce plastics and carbon fiber. The aqueous solvent (water, acid and some solvent) is recycled in the next recycle. Depends on the applied temperature and pressure, during the fractionation process over 60% of the total C5 sugars can be converted to furfural which is collected in the butanol after distillation from the liquor. The organic acids

from the woody biomass feedstock are partially captured in the form of esters and collected with solvent after a simple distillation process.

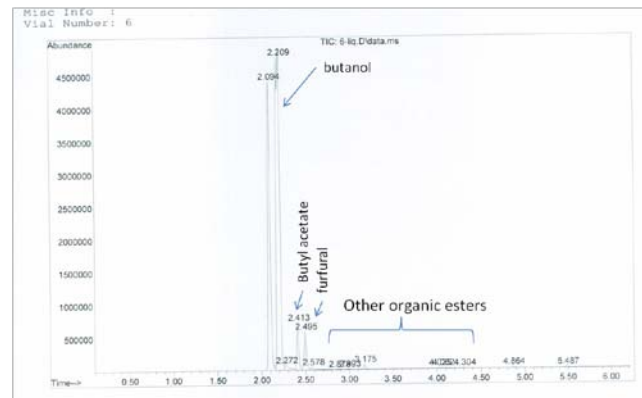


Figure 7: GC profile of liquor obtained from pilot scale organosolv fractionation of wood biomass feedstock. This process not only produces high quality C6 sugar syrup but also in situ converts the C5 sugars to furfural and organic acids to esters. Production of these chemicals in a single step process makes it one of the potential processes to drive sugar economy.

Sugar Production: Sugar production process was optimized in a small scale shake flask by rapid screening process. Organosolv fiber was used as the feedstock for this rapid screening process. Several process factors such as type of enzyme, mixed enzymes, reaction time, pH, time, mixing, solid loading are screened. Several commercial enzymes such as Ctec 2 (Novozymes); HTec2 (Novozymes) GC220 (Genencor); ACC1500 (Genencor); and Speczyme (Genencor) has been tested. Amongst these screened enzymes Ctec2 was found to be the most economical enzyme to produce lignocellulosic sugar syrup. The best process obtained from the rapid screening process was scaled up on a 150L hydrolysis unit using few Kg fiber under mild conditions (45-50C; pH 5-5.5). The sugar syrup produced using the organosolv cellulose was found (by GCMS analysis) to be free from inhibitors for fermentation process. We also developed a multi-step feeding technology to produce more than 20% pure concentrated sugar syrup. By the help of our partners we evaluated that this organosolv sugar syrup is suitable for the production isoprene, ethanol, butanol and lactic acid.

4. SUGAR ECONOMY AND ORGANOSOLV PROCESS

From our economic evaluation; cost of cellulose and enzyme are the major key players to decide the fate of sugar economy. Cellulose from sulfite and Kraft sources that are typically used for paper manufacturing are around \$800/dry ton. At this cost these cellulosic feedstocks does not fit to the sugar economy. The paper pulp manufacturing has been optimized over the year to produce long fibers in expense of

all other ingredients of the biomass. As a result, these processes do not produce any other value added products which may give some hope to reduce the cost of cellulose. On the other hand, the 2nd generation Organosolv pretreatment process discussed here produces shorter fibers (that typically are not useful for paper industries) and several other valuable chemicals that can increase profitability and reduce the overall cost of sugar to its current market value (set by corn and cane). In addition, since the cellulose produced by AST's processes is having short fibers that react much better with enzyme, has allowed us to decrease the use of expensive enzyme and therefore increase the process profitability to make sugar.

5. CONCLUSIONS

Fractionation of woody biomass to cellulose and enzymatic hydrolysis of cellulose to high purity concentrated sugar syrup are demonstrated in pilot scales. In addition to low cost sugar production this process also produces several value chemicals in high yield. This multi-product process shows enormous potential to compete with petrochemical industry and a sustainable sugar economy.

6. REFERENCES

[1] Lynd LR, Wyman CE, Gerngross TU., (1999), Biocommodity engineering. *Biotechnol Progr* 15:777–793.

[2] D.F. Guay, E.L. Singaas “Lignin-Solvent Fuel and Method and Apparatus for Making Same” US patent application 20090145021.

[3] Lee, Y. H., Robinson, C. W., Moo-Young, M., Evaluation of organosolv processes for the fractionation and modification of corn stover for bioconversion, *Biotechnol Bioeng*, 1987, 29(5):572-81

[4] C.V. Stevens, R. Verhe “Renewable bioresources scope and modifications for non-food applications, England: John Wiley and Sons Ltd.:2004.

[5] Claassen PAM, van Lier JB, Contreras AML, van Niel EWJ, Sijtsma L, Stams AJM, de Vries SS, Weusthuis RA. (1999), Utilization of biomass for the supply of energy carriers. *Appl Microbiol Biotechnol* 52: 741–755.

[6] Pan, J.F. et al., Organosolv ethanol lignin from hybrid poplar as a radical scavenger: relationship between lignin structure, extraction conditions, and antioxidant activity, *J. Agric. Food Chem.*, 2006, 54 16 5806-5813

[7] Luis F. Del Rio, Richard P. Chandra, Jack N. Saddler, (2010) The Effect of Varying Organosolv Pretreatment Chemicals on the Physicochemical Properties and Cellulolytic Hydrolysis of Mountain Pine Beetle-Killed Lodgepole Pine, *Appl Biochem Biotechnol*, 161:1-21

[8] Xuejun Pan, Claudio Arato, Neil Gilkes, David Gregg, Warren Mabee, Kendall Pye, Zhizhuang Xiao, Xiao Zhang, John Saddler, (2005), Biorefining of Softwoods Using Ethanol Organosolv Pulping: Preliminary Evaluation of Process Streams for Manufacture of Fuel-Grade Ethanol and Co-Products, *Biotechnology and Bioengineering*, Vol. 90, NO. 4, May 20

[9] Merino, S. T., Cherry, J., (2007). Progress and Challenges in Enzyme Development for Biomass Utilization, *Advances in Biochemical Engineering/Biotechnology*, 108, 95-120

[10] S. Kubo, J.F. Kadla, (2004), Poly(ethylene oxide)/Organosolv Lignin Blends: Relationship Between Thermal Properties, Chemical Structure, and Blend Behavior, *Macromolecules*, 37: 6904–6911

[11] Esa Muurinen, Organosolv Pulping a Review and Distillation Study Related to Peroxyacid Pulping, PhD Thesis, 2000