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# FUEL ALCOHOL

## FUEL ALCOHOL: CELLULOSE CONVERSION TECHNOLOGY

### Introduction

Various estimates place the amount of waste cellulose (crop residue, wood wastes, etc.) at approximately one billion tons per year. At least half of this amount is "collectable biomass" that could be used as alternative energy sources. One technique is to convert the cellulose waste into fermentable sugars for the production of alcohol fuels. Until recently, this conversion was uneconomical due to the difficulties and low yields in the hydrolysis of the cellulose. What follows is a brief description of work done at Purdue University's Laboratory of Renewable Resources Engineering by George T. Tsao and Michael Ladish. They have developed a pretreatment in which selective solvent extraction is used to fractionate the cellulose waste into its three individual components: cellulose, hemicellulose, and lignin. Once the cellulose is dissolved in a solution, it is no longer protected by its crystalline structure nor a lignin seal. The reprecipitated cellulose can then be easily hydrolyzed by either acids or enzymes to yield high levels of glucose. Hydrolysis is the process by which the bond between the monosaccharides is broken by using either hydronium (hydrogen) ions or enzymes as catalysts.

### General Background

Cellulose is a homogeneous polymer of glucose. Hemicellulose molecules are, for the most part, polymers of pentoses (xylose and arabinose), hexoses (mannose), and a number of sugar acids. Lignin is a polyphenolic macromolecule. Hydrolysis of hemicellulose to mono- and oligo-

saccharides is a comparatively easy matter using either acids or enzymes. On the other hand, cellulose is strongly resistant to hydrolysis.

Table 1. Composition of Various Cellulose Sources

	Farm Crop Residue	Corn Cobs	Soft Woods
Cellulose	34%	40%	42%
Hemicellulose	40%	36%	25%
Lignin	20%	16%	28%

### Cellulose Hydrolysis

Cellulose is a linear homopolymer of anhydroglucose units linked together with 1,4-beta-glucosidic linkages. The difficulties encountered in hydrolysis are: (1) a highly ordered crystalline structure, and (2) a lignin seal surrounding cellulose fiber forming a physical barrier.

In practice, the 1,4-beta-glucosidic linkage is no more difficult to break than the 1,4-alpha-glucosidic linkage in starch if the molecules are fully hydrated and exposed and free from hindrance due to the lignin seal and crystalline structure.

The easily hydrolyzable portion of cellulose is often referred to as the "amorphous" region of cellulose and the resistant residue as the crystalline cellulose. On the average, cellulose is 15% amorphous and 85% crystalline. Crystalline cellulose requires a strong acid at high temperatures to hydrolyze. These conditions also cause decomposition of the glucose products into undesirable degradation by-products.

Keeping in mind the two factors, (1) the strong crystalline structure, and (2) the lignin seal, one can readily understand the difficulties involved in cellulose hydrolysis. The two techniques normally employed for hydrolysis are acids and enzymes. Acids are nonspecific catalysts and attack cellulose as well as lignin. Unfortunately, due to the strong crystalline nature of cellulose, only very concentrated acids can hydrolyze cellulose to a sufficiently high degree. The resulting costs for equipment, acids, and alkali for subsequent neutralization are extremely high. These costs, plus its tendency to decompose glucose into undesirable by-products, limit its commercial application.

Enzymes, on the other hand, are specific catalysts. The enzyme cellulase can readily convert cellulose into glucose. The problem is the non-accessibility of the macro-molecular enzyme to the cellulose fibers due to the lignin seal. To overcome this problem, cellulose can be milled to break the lignin seal. The resulting cellulose is then readily hydrolyzed by cellulase. However, the cost of milling cellulose is prohibitively high and hydrolysis is not yet a commercially successful technique.

#### **Pretreatment by Solvent**

Research at Purdue University has developed a technique of solvent pretreatment to selectively extract cellulose and thus allow hydrolysis free from the obstacles previously described. Three solvents have been successfully used in pretreatment (Cadoxen, CMCS, and sulfuric acid). The cellulose is first dissolved in the solvent and then reprecipitated out as a soft floc. In this form it is readily hydrolyzed, using either cellulase enzymes or acids, with high conversion efficiency to glucose.

#### *Cadoxen as a Cellulose Solvent*

Cadoxen or tris (ethylenediamine) cadmium hydroxide is a clear, colorless, nearly odorless liquid, that is stable for long periods of time and causes little degradation of cellulose. Its com-

position includes 25 to 30% ethylenediamine in water and 4.5 to 5.2% cadmium (added as oxide or hydroxide) based upon the total liquid weight. Cadoxen is considered a useful solvent for several reasons:

- (1) It contains 70 to 75% water and thus no pre-drying of the cellulose material is required.
- (2) Cadoxen can dissolve some 10% by weight of cellulose at room temperature.
- (3) It is stable at room temperature.
- (4) It is nontoxic to cellulase enzymes.

Cadoxen pretreatment increases glucose yields by as much as a factor of four over untreated residues.

#### *CMCS as Solvent Pretreatment*

CMCS is less toxic than cadoxen and thus easier to handle. CMCS is an aqueous solution of 17% sodium tartrate, 6.6% ferric chloride, 7.8% caustic, and 6.2% sodium sulfite. The solvent can be made in either a liquid or solid form by treatment with methanol. The cellulose is readily dissolved in CMCS and can be reprecipitated with the addition of water or methanol. Yields of up to 90% glucose have been obtained from corn residues using CMCS and cellulase enzymes.

#### *Concentrated Sulfuric Acid*

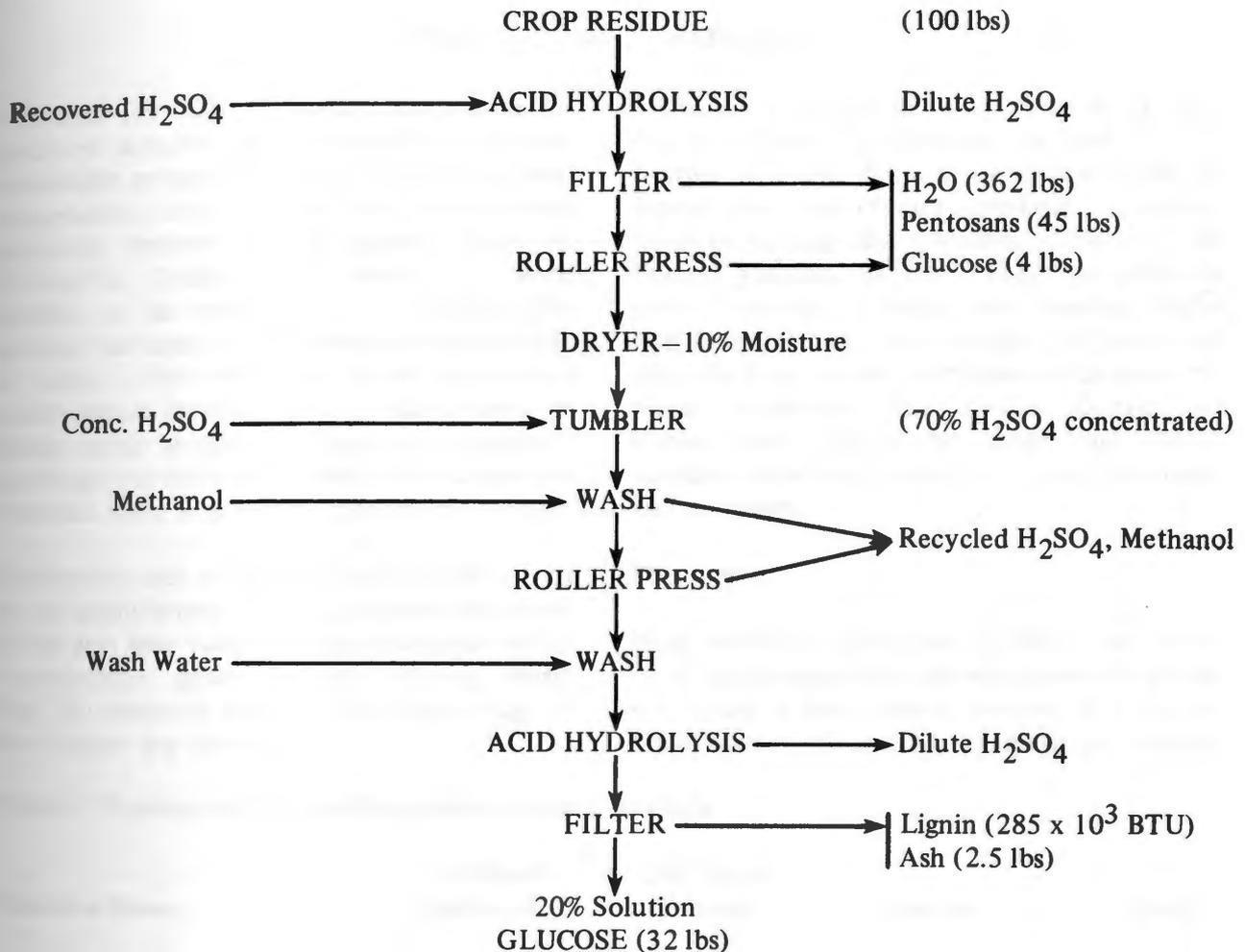
Sulfuric acid can be used as both a solvent and a catalyst for hydrolysis. A dilute acid is first used to hydrolyze and remove the hemicellulose and a small percentage of the amorphous cellulose. The solid residue is then dried to a 10% moisture, and 70% sulfuric acid is added with strong mixing and tumbling. Methanol is then added to dilute the mixture and reprecipitate the cellulose. After filtration, water is used to dilute the mixture and the solid residue is hydrolyzed with dilute sulfuric acid to yield glucose. The filtrate and wash waters are recycled. Laboratory results show a better than 90% yield of glucose with dilute sulfuric acid hydrolysis.

A more detailed flowsheet of a process using sulfuric acid is shown in Figure 1. A process

employing sulfuric acid has the best short-term potential for commercial application. Conversion efficiency of 80% or more is projected, which results in slightly more than 100 gallons of ethanol per ton of cellulose waste.

### Bibliography

Tsao, George T., et al. "Fermentation Substrates from Cellulosic Materials: Production of Fermentable Sugars from Cellulosic Materials." *Annual Reports on Fermentation Processes*, Vol. 2, Academic Press, Inc., 1978.



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