GLUCOSE FROM PAPER MILL SLUDGE

Sujit Banerjee

Enzymatic hydrolysis of sludge from a bleached tissue mill generates glucose that can be sold as a product or sent to an ethanol plant. Hydrolysis rates using enzymes from two sources are reported, and a configuration for the industrial conversion of sludge to glucose is proposed. The system combines a set of stirred tank reactors with ash removal and membrane filtration to give a glucose concentrate. The economics of the conversion are attractive.

Keywords: Cellulase; Sludge; Economics; Glucose; Sludge

Contact information: Institute of Paper Science & Technology, School of Chemical & Biomolecular Engineering, Georgia Tech, Atlanta, GA 30332-0620 USA; E-mail: sb@gatech.edu

INTRODUCTION

The production of ethanol from biomass is an international priority, and major initiatives are underway to improve the cost:benefit ratio for this process. Work on cellulosic biomass typically focuses on wood chips pre-treated to increase accessibility of the cellulose to the enzyme (Silva et al. 2011; Kumar et al. 2009). Switchgrass and other biomass are also being considered as feedstocks (Schmer et al. 2008; Epplin 1996). Cellulosic sludge is a particularly attractive raw material because of its negative value; a cost is incurred for its disposal. Several proposals have been made for its beneficial use (Vamvuka et al. 2009; Sterner and Ferguson 2001; Van Ham et al. 2009; Laubenstein 2004; Allen 2003; Carroll and Reeves 1999), but few of these have been implemented on a large scale.

The concept of using paper mill sludge as a feedstock for ethanol production has been explored by Lee and coworkers (Kang et al. 2010, 2011). However, the amount of ethanol that can be potentially produced at each mill is relatively small when compared to that made in a typical corn ethanol plant, and construction of an ethanol plant at each paper mill site may be difficult to justify economically.

The proposition developed in this paper is to convert the cellulosic fraction of sludge to glucose and to then either sell the glucose or send it to a dedicated operation (such as a corn ethanol facility) for conversion to ethanol. Alternatively, the glucose and other organics can be anaerobically converted to methane, but the capital costs are relatively high, which makes the economics unattractive, especially in light of the present low cost of natural gas. The enzyme required for the hydrolysis is the most expensive consumable, and much effort is being directed towards bringing down its cost. In one approach, retention aids used in the paper industry can serve as enzyme accelerators and reduce the dosage of the enzymes (Reye et al. 2009, 2011; Mora et al. 2011).

EXPERIMENTAL

Pressed sludge from a tissue mill was received on November 2009 and on January 2010. Its carbohydrate content was measured after a two-stage acid hydrolysis followed by high performance anion exchange chromatography with pulsed amperometric detection (NREL 2008). The results are reported in Table 1 as weight percent on an oven-dry solids basis. The ash content of the November and January sludges was 3.3 and 4.9 wt %, respectively. The ash represents a deadload, and a low-ash feedstock has better economics. The maximum potential yield of glucose resulting from hydrolysis is [glucan] x 1.11 (NREL 2008), or 56% and 64%, respectively, for the two sludges. Only sludge from the November collection was used in this study; the January values are provided to demonstrate that the sludge composition is relatively stable over time.

Table 1. Carbohydrate Content of Sludge (wt %)

	November 2009	January 2010
Glucan	50.9	57.8
Xylan	9.9	9.5
Mannan	2.8	2.3
Arabinan	0.3	0.2
Galactan	0.3	0.2
Total	**64.2**	**70.0**

Two enzymes were used: Cellic Ctec from Novozymes and Optimase CX 15L from Genencor. Both were state of the art products at the time of the trial; more efficient and cost-effective enzymes have been subsequently introduced.

Hydrolysis was conducted in a 2.5 l Bioflo 3000 reactor or in shake flasks. For the former, the sludge was diluted to 5% (dry basis) and suspended in the reactor at 50 ^{o}C and disinfected with 600 ppm NaOCl for 20 minutes. Disinfection is essential for forestalling consumption of the glucose by microorganisms present in the sludge, and also for odor control. The suspension was vigorously stirred with the enzyme. Although the temperature was set at 50 ^{o}C, temperature control is not always necessary. The rate of hydrolysis of the fines fraction of sludge increases with temperature, but that of the longer fiber is relatively temperature-independent (Lu et al. 2010). Hence, sludge containing a high proportion of long fibers can be processed at room temperature.

The pH was adjusted to 4.8 with HCl and chloramine-T added to a final concentration of 10 ppm to maintain sterility. The activity of the Novozymes enzyme was 84 FPU/mL; that of the Genencor product was 46 FPU/mL. Glucose was determined with the GOPOD method (Megazyme 2010) automated with a DA3500 Discrete Analyzer from OI Corporation, College Station, TX. The sample was filtered through a 0.2 µm filter prior to analysis. The average error from duplicate measurements was 4.5%. Shake flask experiments were run in 125 mL flasks in a 50^{o}C water bath. The other steps were the same as those described above.

RESULTS AND DISCUSSION

Hydrolysis in Shake Flasks

The effect of enzyme loading on the rate of hydrolysis of sludge is shown in Fig. 1. The final consistency was between 1.64 and 1.94%, which is a significant drop in solids from the initial 5%. From Fig. 1 the rate dependence on the enzyme concentration was empirically found to be,

$$rate_1/rate_2 = \{[enzyme_1] / [enzyme_2]\}^{0.44} \quad (1)$$

where $rate_1$ and $rate_2$ are the rates corresponding to any two enzyme doses. In other words, the rate only rises by 35% when the enzyme concentration is doubled. The practical importance of this finding is that it allows one to balance the cost of the enzyme against the value of the product. The value of new technology that boosts the rate of enzymatic hydrolysis can be more precisely evaluated.

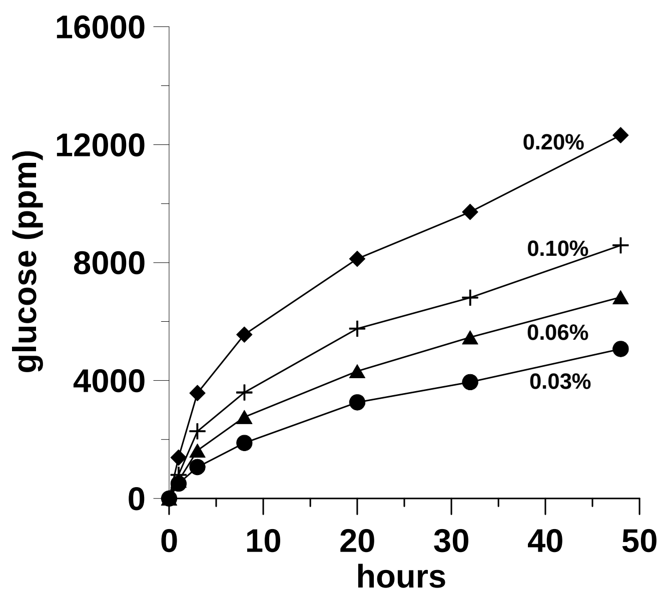

Fig. 1. Effect of enzyme (Novozymes) dose on the rate of hydrolysis of sludge

Hydrolysis in a Bioreactor

Glucose production from sludge hydrolysis in the 2.5 L bioreactor by the Novozymes and Genencor enzymes is illustrated in Figs. 2 and 3, respectively. The Genencor cellulase (46 FPU/mL) was added at 0.18%, which equals the same total activity used for the Novozyme enzyme, which was added at 0.1% cellulase (84 FPU/mL). The results are similar and must be evaluated in light of the costs of the enzyme. Overall, the results in Figs. 2 and 3 are in broad general agreement with those in Fig. 1, confirming our expectation that the results are independent of the experimental configuration, *i.e.* shake flask *vs.* a bioreactor.

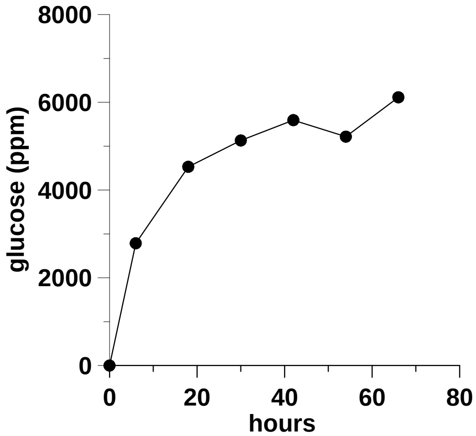

Fig. 2. Hydrolysis of sludge by the Novozymes enzyme

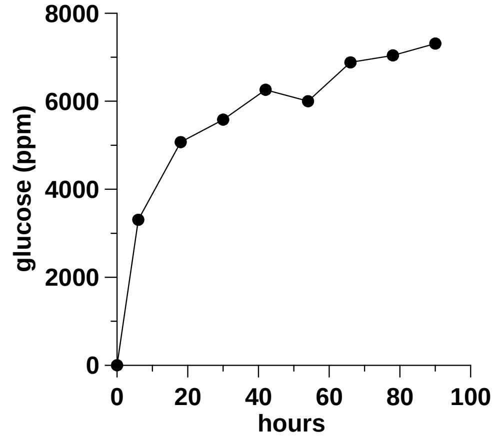

Fig. 3. Hydrolysis of sludge by the Genencor enzyme

Conversion of Cellulosic Sludge to Glucose

A schematic for the conversion of the cellulose in sludge to glucose is presented in Fig. 4. The hydrolysis is conducted in a series of CSTRs with the inert solids being removed either in a settling tank (as shown) or with a centrifugal cleaner. The glucose is concentrated through membrane filtration and the water recycled. The economics are conservatively based on a reverse osmosis membrane, although it is possible that less expensive ultrafiltration will suffice. Water recycling and glucose concentration is important to minimize water disposal costs and to reduce the volume of material to be transported to a downstream facility for conversion of the glucose to ethanol. The main conclusion from this aspect of the study is that the fibrous components of sludge can be enzymatically converted to glucose, which can be sold as such or sent to an ethanol plant for fermentation to ethanol.

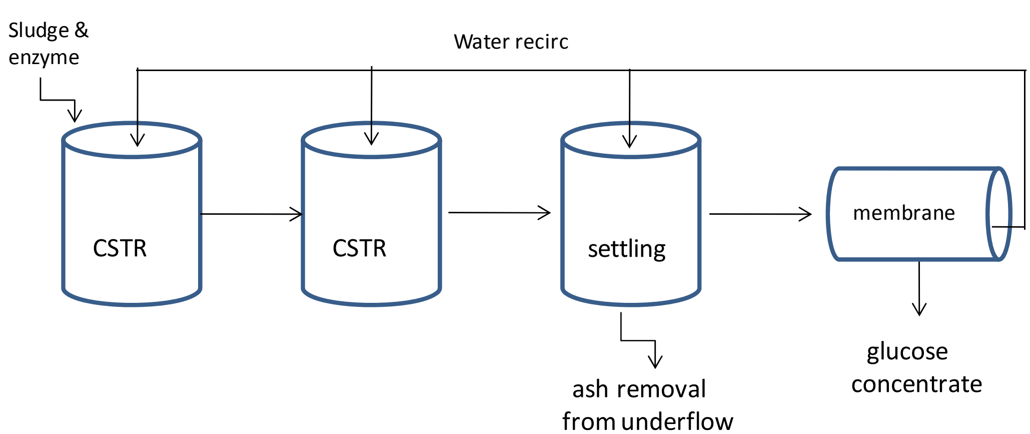

Fig. 4. Conceptual schematic for the conversion of the cellulosic component of sludge to glucose

The economics are based on sludge containing 50 tonnes per day of cellulose. The actual sludge mass will be higher due to the presence of filler and other non-cellulosic materials. Hydrolyzing high ash or lignin-containing sludge will be more expensive on account of the non-cellulosic deadload and because the cellulose will be less accessible to the enzyme. A sludge consistency of 5% is assumed because that was the amount actually used in this study. A much higher consistency can be achieved with high intensity mixers common in paper recycling, in which case the costs would drop substantially.

The enzyme is the major cost, and the glucose recovered is the principal benefit; both costs are volatile. Ideally, one would use the costs associated with enzyme and glucose to calculate the cost:benefit ratio. However, while the glucose value is available from a referenced source (USDA 2011), a standard cost for the enzyme is not available. Hence the costs for all the other variables were calculated, and the maximum cost of the enzyme that would allow a break-even proposition was estimated. The actual cost of the enzyme would need to be lower than this maximum in order for the process to be economically viable.

The assumptions and projections are summarized in Table 2. Water treatment is estimated at $1,100 per day (including capital and O&M) and it is assumed that reverse osmosis will be needed. The value of the glucose produced (assuming 80% conversion from fiber) is about $20,000 per day. The value of sludge disposal avoidance is taken at $3,000 per day for a total benefit of $23,000 per day. Sludge disposal costs can vary widely depending on location; the value used is typical of a mill in Georgia. The capital required will be in-ground tanks, pumps, agitators, and dewatering equipment to handle the residual solids; the amortized cost is estimated at $500/day. Other costs are acid and power; these are small compared to the other costs and are neglected.

Although the value of the glucose is assigned the value of raw sugar syrup, it may not be possible to realize this value, because it originates from sludge and there will likely be a bias against using a sludge-derived product in foodstuff. The purity should not be an issue as it will be membrane filtered, but the negative perception may be difficult to overcome. Two non-food applications may be considered. One, the glucose could be converted to ethanol in a conventional corn/ethanol facility. The amount of glucose obtained from 50 tonnes of sludge is very small compared to the total load processed by the plant and it can be easily accommodated. However, there will be a transportation cost incurred because paper mills are not usually located near corn/ethanol facilities. The other option is to construct a dedicated plant for converting sludge glucose to ethanol that is capable of accepting glucose from several neighboring facilities.

If the equivalent of the Novozymes enzyme is considered at a dosage of 0.03% (by volume), then 300 kg would be required to treat 50 tonnes of sludge at a consistency of 5%. The break-even cost of the enzyme would be $72/kg. The actual present cost is about fortyfold lower, so if the assumptions in Table 2 are accepted, then the conversion of sludge to glucose is an attractive value proposition. The value of the glucose is the largest factor in the economics. However, the proposition is attractive even if the value of the glucose is several times lower than that used in Table 2. Furthermore, it is safe to assume that the cost of sludge disposal will continue to rise. The cost of the enzymes has been dropping continuously, which means that the cost:benefits of the process will continue to improve, as both the numerator and denominator will be favorably impacted.

Table 2. Economics of Converting Sludge to Glucose

Costs/day

Enzyme: to be estimated

Water treatment (RO): $1,100 (includes capital & O&M)

Capital: In-ground tanks, pumps, agitators, dewatering equipment (installed): $1MM - $2MM with safety factor. The cost/day for a 20-year amortization schedule at 8% is about $500.

Other costs (negligible): acid, power, etc.

Benefits/day

Glucose: $20,000 (assuming 66¢/kg raw sugar syrup, June 2011 value from USDA 2011 and 80% sludge conversion)

Sludge handling/landfill avoidance: $3,000

The favorable economics apply only to a "best case" sludge, *i.e.* one composed of short bleached fiber and only a small quantity of ash. The rate of hydrolysis of brown fibers in sludge from a brown mill will be much slower. The high ash content of recycle sludge makes for a high deadload and also a large amount of inert residual material that has to dewatered again before disposal. The economics developed here are "first-cut" and are intended to demonstrate qualitative cost:benefits. The variables inherent in the cost:benefits analysis need to be recognized; for example, the cost of raw sugar syrup varied over a factor of two in 2010 (USDA 2011). The purpose of this economic analysis is to highlight the fact that the conversion of sludge to glucose can be an attractive economic proposition, but that the sensitivities need to be taken into account.

CONCLUSIONS

1. Enzymatic hydrolysis of sludge from a bleached tissue mill leads to glucose that can be sold as a product or sent to an ethanol plant.
2. The hydrolysis rate was non-linear with enzyme concentration under conditions used.
3. A configuration for the industrial conversion of sludge to glucose is proposed.
4. The cost:benefits of the conversion are attractive.

ACKNOWLEDGMENTS

The study was funded by the Traditional Industries for Pulp and Paper (TIP^3) program of the State of Georgia. I thank Tuan Le for laboratory work and the members of the TIP^3 industrial advisory committee (especially Robert Sackellares) for its comments, especially on the economics. I am grateful to Novozymes and Genencor for several gifts of cellulase.

REFERENCES CITED

Allen, M. (2003). "Beneficial use of secondary fiber residual," TAPPI Environmental Conference.
Carroll, T. W., and Reeves, W. L. (1999). "Glass aggregate technology turns mill sludge into useful product," *Pulp and Paper* 73(4), 79-86.
Epplin, F. M. (1996). "Cost to produce and deliver switchgrass biomass to an ethanol-conversion facility in the southern plains of the United States," *Biomass Bioenergy* 11(6), 459-467.
Kang, L., Wang, W., and Lee, Y. Y. (2010). "Bioconversion of kraft paper mill sludges to ethanol by SSF and SSCF," *Appl. Biochem. Biotechnol.* 161(1-8), 53-66.
Kang, L., Wang, W., Pallapolu, V. R., and Lee, Y. Y. (2011). "Enhanced ethanol production from de-ashed paper sludge by simultaneous saccharification and fermentation and simultaneous saccharification and co-fermentation," *BioResources* 6(4), 3791-3808.
Kumar, P., Barrett, D. M., Delwiche, M. J., and Stroeve, P. (2009). "Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production," *Ind. Eng. Chem. Res.* 48(8), 3713-3729.
Laubenstein, J. (2004). "Beneficial use of short paper fiber (paper mill sludge) for pollution prevention in the mining industry," TAPPI Paper Summit - Spring Technical and International Environmental Conference.
Lu, J., Reye, J., and Banerjee, S. (2010). "Temperature dependence of cellulase hydrolysis of paper fiber," *Biomass Bioenergy* 34, 1973-1977.
Megazyme (2010). "D-glucose assay procedure (GOPOD-format) K-GLUC 03/2010," Wicklow, Ireland.
Mora, S., Lu, J., and Banerjee, S. (2011). "Mechanism of rate enhancement of wood fiber saccharification by cationic polyelectrolytes," *Biotechnol. Lett.* 33, 1805-1808.
NREL (2008). "Determination of structural carbohydrates and lignin in biomass," Laboratory Analytical Procedure, National Renewable Energy Laboratory Technical Report NREL/TP-510-42618.
Reye, J. T., Maxwell, K., Rao, S., Lu, J., and Banerjee, S. (2009). "Cationic polyacrylamides enhance rates of starch and cellulose saccharification," *Biotechnol. Lett.* 31, 1613-1616.
Reye, J. T., Maxwell, K., and Banerjee, S. (2011). "Cationic polyacrylamides promote binding of cellulase and amylase," *J. Biotechnol.* 154, 269-273.
Schmer, M. R., Vogel, K. P., Mitchell, R. B., and Perrin, R. K. (2008). "Net energy of cellulosic ethanol from switchgrass," *Proc. Natl. Acad. Sci.* 105(2), 464-469.
Silva, N. L., Betancur, G. J., Vasquez, M. P., Gomes Ede, B., and Pereira, N. Jr. (2011). "Ethanol production from residual wood chips of cellulose industry: acid pretreatment investigation, hemicellulosic hydrolysate fermentation, and remaining solid fraction fermentation by SSF process," *Appl. Biochem. Biotechnol.* 163(7), 928-936.
Sterner, P., and Ferguson, L. (2001). "Beneficial reuse of deinked office waste sludge," 6th Research Forum on Recycling, Proceedings, 213-217.
USDA (2011). "World and U.S. sugar and corn sweetener prices," http://www.ers.usda.gov/briefing/sugar/data.htm

Vamvuka, D., Salpigidou, N., Kastanaki, E., and Sfakiotakis, S. I. (2009). "Possibility of using paper sludge in co-firing applications," *Fuel*, 88, 637-643.

Van Ham, M., Dampier, L., Morton, K., and Mullen, S. (2009). "Pulp and paper sludge as a barrier layer in landfill closure: A new opportunity," *Pulp and Paper Canada*, 110, 25-30.

Article submitted: August 16, 2011; Peer review completed: September 24, 2011; Revised version received and accepted: September 28, 2011; Published: September 30, 2011.