Research on

BIO-CHEMICAL CONVERSION OF BIOMASS

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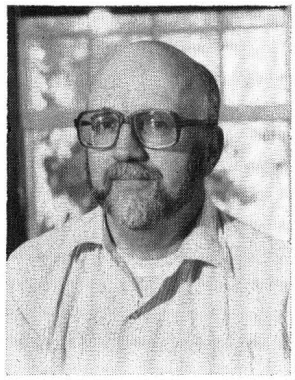
THE OBJECTIVE OF OUR WORK is to contribute to the development of new practical processes for the conversion of the cellulose found in biomass to fuels, chemicals, and foods. Industrial scale plants for the dilute acid catalyzed hydrolysis of the cellulose in wood are currently operated in USSR, and in the past both concentrated HCl and dilute H_2SO_4 processes have been developed in Europe and the USA. However, these processes have not been commercially viable in competition with petrochemicals and soybean protein.

ACID HYDROLYSIS

Our work in this area began in 1967 when Andrew Porteous, then a student in the DE program, recommended in the solution to his qualifying examination (a design problem on which the student has 30 days to work) that a continuous plug flow reactor be used to carry out dilute acid hydrolysis of the cellulosic material found in municipal wastes. Compared to the percolation reactor that had been developed for woody materials by the Forest Products Laboratory at Madison, Wisconsin [10], Porteous reasoned that the plug flow reactor would be able to handle materials, such as waste paper, that would not be porous enough for percolation, and furthermore the process would be fully continuous [9]. The kinetics for Douglas fir [10] indicated that the yield of glucose would increase as the temperature is increased and the residence time is reduced. This is of particular importance because the yields obtainable in a percolation reactor are inherently greater than in a plug flow reactor.



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Obviously the costs and corrosion problems associated with higher temperatures limit the practical temperature, and mixing and heating requirements established a lower limit on the residence time.

With support from EPA, Fagen [2], for his ME thesis, conducted batch hydrolysis experiments and measured the kinetics constants for paper, the principal cellulosic component of municipal wastes. He found that they were similar to those for Douglas fir and hence a plug flow reactor should be operated at high temperature and a short residence time. Subsequent studies on many biomass substrates have shown this conclusion to hold true in general.

Obviously the costs and corrosion problems associated with higher temperatures limit the practical temperature, and mixing and heating requirements established a lower limit on the residence time. Hence, we set out to develop a flow reactor to determine the yields that could in fact be obtained. From a more scientific point of view, the flow reactor has another attraction: it allows one to study the kinetics of hydrolysis under more severe conditions than can accurately be studied

in a batch reactor because short residence times can be obtained without the heat up transients involved in a batch reactor.

Lay [6], Thompson [11], and McParland [8] (supported first by NSF and later by DOE), in their respective ME theses, developed the present flow reactor, shown in Fig. 1, and studied the kinetics of several substrates. Currently the acidified slurry is pumped into the reactor along with high pressure steam which condenses, mixes with, and heats the mixture to reaction temperature in, we estimate, about 0.7 sec. The minimum residence time used thus far is 7 sec. and the maximum temperature, 260 C. Under these conditions the glucose yield is 55-60%. Current modifications should permit operation at 280 C where a 70% yield is expected.

Several other approaches are being taken in an effort to increase the yield from acid hydrolysis. The glucose yields are reduced by the fact that glucose decomposes under the same conditions as it forms. Ward is currently studying whether the presence of acetone, through the formation of glucose-acetone complexes, can be used to reduce the glucose decomposition. Holland is currently designing a reactor which is to have a shorter residence time for the liquid, and hence less glucose decomposition, than for the solids. Vick Roy [12] has recently explored the use of SO_2 catalyzed hydrolysis under supercritical conditions.

Because of the difficulty in pumping slurries containing a high concentration of wood, and the practice of injecting live steam into the flow reactor, the sugar concentrations in the reactor effluent are low. By using a nonaqueous immiscible carrier fluid in place of water, we have found it possible to increase the concentration of sugar in the aqueous phase. This also permits another means for separating the products. Woods have small amounts of rosins and oils, and they would be expected to concentrate in the nonaqueous phase. Of course, these advantages must justify the cost of any carrier fluid which is not recovered as well as additional processing steps. Further study is needed to allow such evaluation.

ENZYMATIC HYDROLYSIS

As an alternative to acid catalyzed hydrolysis, enzymes can be used to catalyze the reaction. In this case, the glucose yields, with proper pretreatment of the substrate, are in the range of 95-100%, considerably higher than is obtained with acid hydrolysis. The reaction, however, is much slower; 24-48 hrs. rather than 7 sec. Grethlein [3] compared these two methods, using data from Berkeley [13], and concluded that at that time acid hydrolysis appeared more attractive. This process evaluation is currently being updated through a set of process studies sponsored by DOE/SERI.

In her DE thesis, Knappert [4] (with support from NSF and International Harvester Corp.), showed that by operating the flow reactor under somewhat milder conditions (1% H_2SO_4, 7-10 sec., 200 C) an effective pretreatment could be obtained. Upon enzymatic hydrolysis of these pretreated solids, the glucose yield was >90% in 24 hrs. compared to 35% in 48 hrs. from unpretreated solids. Knappert showed that this pretreatment

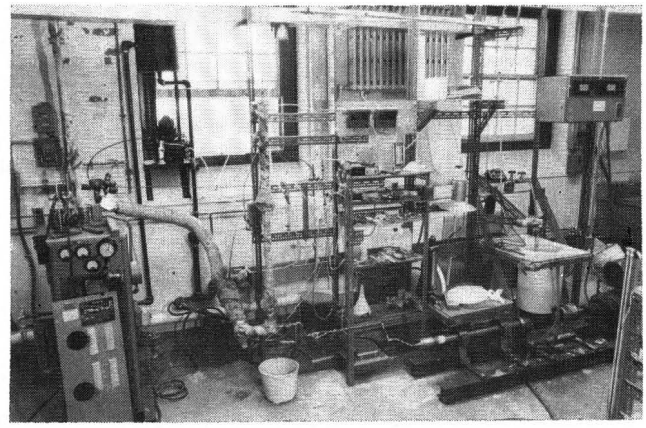

FIGURE 1. Flow reactor equipment.

increases the fraction of pores that are larger than the enzyme molecule. Subsequent studies by Allen [1] and others have shown that the crystallinity of the cellulose remains unchanged and that the lignin is not removed. The pores are increased by the removal of a fraction of the hemicellulose, and contrary to the prevailing view, we now believe this to be the essential feature of an effective pretreatment. Grous is currently extending this study to include other methods of pretreatment.

BYPRODUCTS

Although glucose is the principal sugar (maximum yield = 42% of dry hardwood), a significant amount of xylose can be produced (maximum yield = 18% of dry hardwood). Whereas glucose is easily fermented to ethanol, xylose is not. Naturally, efforts are underway at a number of laboratories to develop yeasts than can effectively carry out such a fermentation. However, xylose can be used to produce single-cell protein. Furthermore, its decomposition product, furfural, has a con-

These theses include both process design and development, and basic research in applied science, in keeping with our two sets of graduate degrees . . .

siderable value, albeit to a small market. In his PhD thesis, Kwarteng [5] (supported by Dow Chemical Co. and DOE/SERI), reformulated Root's kinetic model for the formation and decomposition of furfural from xylose, and redetermined the constants from experiments in the flow reactor. He also extended the model to include the formation of xylose from the xylan in the biomass. In contrast to xylose and glucose decomposition, furfural decomposition is second order. Hence, the furfural yield is increased by using a more dilute feed. This is countered by acid costs, product concentration, and heating costs, all of which favor a more concentrated feed. Process optimization studies are underway to evaluate the optimum feed concentration of biomass. Even at half the current market price furfural is two to three times more valuable than the sugars produced; hence its production could have an important impact on the profitability of the overall process.

Lignin is another byproduct that we plan to study in the future. Some of it is solubilized in the flow reactor, and the solubility of the residue in solvents is increased. Furthermore, the short residence time followed by flash quenching employed in the flow reactor is expected to give it unique properties.

PRODUCT SEPARATION

The overall process has three main parts: hydrolysis of the biomass to produce sugars and furfural, fermentation of the sugars to ethanol or possibly other chemicals, and separation of the ethanol to an anhydrous product if the ethanol is to be added to gasoline. Even though it requires a considerable amount of energy, distillation still appears to be the preferred means of separation. In his ME thesis, Lynd [7] proposed a new means of combining heat pumps with distillation that significantly reduces the energy requirement, particularly for dilute feeds which are usually encountered when fermentation is used to generate the feed.

The azeotrope formed between ethanol and water makes their separation more difficult, and even if a salt such as potassium acetate (KAc) is added to break the azeotrope, with normal distillation the reflux (and hence energy) must remain high if the feed is dilute, e.g. 1-10 wt. %. Lynd's innovation helps to overcome this requirement. Hence, the use of KAc looks much more attractive. Work is getting underway to test out the critical aspects of this process experimentally.

FERMENTATION STUDIES

Tricoderma reesei is a fungus which produces the extracellular enzymes used in our enzyme hydrolysis work described above. It must be grown on a cellulosic substrate in order to produce these cellulase enzymes, but unfortunately can not be present during the main hydrolysis step since it would consume the glucose product. Hence, the enzymes must be produced in a separate step. Since the pretreatment is effective in the hydrolysis step, we are now testing its effectiveness in the kinetics of the enzyme production step.

Some thermophylic bacteria have the ability to ferment cellulose directly to ethanol. As the name implies, they live at relatively high temperatures and hence the likelyhood of contamination of this fermentation by other organisms is low. However, they also have some limitations: they ferment natural biomass, which contains lignin as well as cellulose, very slowly; they have a low tolerance compared to yeast for the ethanol that they produce and hence produce dilute beers, and they produce other products that compete for the substrate. We think that it may be possible to overcome these limitations through the use of mild acid hydrolysis in the flow reactor as a pretreatment, combined with simultaneous fermentation and product removal using Lynd's distillation scheme to remove the ethanol from the dilute beer as it is formed thus altering the product distribution in the favor of ethanol. Lynd will undertake a study of this in his DE thesis.

In order to emphasize the role of the students in this work, the references cited are primarily student theses rather than papers in the literature. These theses include both process design and development, and basic research in applied science, in keeping with our two sets of graduate degrees —ME and DE for those interested primarily in design and MS and PhD for those interested primarily in research. The distinction is one of degree since many theses involve both elements. The undergraduate programs of the students involved in this work have included biology, chemistry, engineering science, and civil engineering as well as chemical engineering, in keeping with non-

departmental organization of the Thayer School. □

REFERENCES

1. Allen, D. C., "Enzymatic Hydrolysis of Acid Pretreated Cellulosic Substrate: Substrate Hydrolysis, Process Development & Process Economics," ME thesis, Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, 1983.
2. Fagan, R. D., "The Acid Hydrolysis of Refuse," ME thesis, Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, 1969.
3. Grethlein, H. E., "Comparison of the Economics of Acid and Enzymatic Hydrolysis of Newsprint," *Biotech Bioeng*, Vol. XX, 503, 1978.
4. Knappert, D. R., "Partial Acid Hydrolysis Pretreatment for Enzymatic Hydrolysis of Cellulose: A Process Development Study for Ethanol Production," DE thesis, Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, 1981.
5. Kwarteng, I. K., "Kinetics of Dilute Acid Hydrolysis of Hardwood in Continuous Plug Flow Reactor," PhD thesis, Thayer School of Engineering Dartmouth College, Hanover, NH 03755, 1984.
6. Lay, J. R., "The Acid Hydrolysis of High Solid Content Cellulose Slurries," ME thesis, Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, 1978.
7. Lynd, L. R., "Energy Efficient Distillation with Innovative Use of Heat Pumps," MS thesis, Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, 1984.
8. McParland, J. J., "The Acid Hydrolysis of Cellulosic Biomass: A Bench Scale System and Preliminary Plant Design," ME thesis, Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, 1980.
9. Porteous, A., "Improved Manufacture of Polyurethane Foam," DE thesis, Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, 1967.
10. Saeman, J. F., "Kinetics of Wood Saccharification," Industrial and Engineering Chemistry, *37*, 32, 1945.
11. Thompson, D. R., "The Acid Hydrolysis as a Means of Converting Municipal Refuse to Ethanol: Process Kinetics and Preliminary Plant Design," ME thesis, Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, 1978.
12. Vick Roy, J. R., "Biomass Hydrolysis with Sulfur Dioxide," ME thesis Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, 1984.
13. Wilke, C. R., R. D. Yang and U. Von Stockar, Biotech. Bioeng. Symp., 6, 155, 1976.

VIDEO-BASED SEMINARS

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and use of non-communicative words such as "uh", etc. Sometimes the review sessions were absolutely devastating for the presenter since these mannerisms are greatly "amplified" by the video camera and, of course, preserved for posterity. However, I was pleasantly surprised by the light-hearted attitude with which all students received the review process. There was much good-natured kidding about the errors, and no one seemed to be embarrassed or hurt by the review.

The two best presentations (i.e. free from errors) were edited, together with my brief comments, into one tape which we shall use as a means of external communication to industry and to other academic institutions. For example, I plan to send this tape to some industry contacts to introduce our research group and to precede my visit to a group I have yet to meet. Secondly, this tape may be used as a subtle recruiting aid at academic institutions which I may visit. Students seem to listen intently to their peers regarding graduate research experiences.

REACTIONS TO THE VIDEO SEMINARS

The student reactions to this new format were varied. Some met the video-based seminar course with enthusiasm, some with fear, and some with indifference. A few were cynical about the value of a seminar course which did not allow a tough question-and-answer session. Many felt that further refinement of their seminar mechanics was unnecessary. The professors showed the opposite feelings, perhaps as a result of years of teaching and giving technical presentations—seminars. However, after the taping all were of the same accord. Moreover, the students became more aware of the original intent of this experiment: to provide a new format which would allow instant feedback on a seminar presentation. The video-based format best satisfies that need for instant feedback.

CONCLUSIONS

In conclusion, this brief experiment with video-based seminars was successful with regard to the original intent of improving visual communication skills in a formal seminar setting. This format is suitable for use as an occasional tool, preferably with students who have had some experience in seminar presentation. We may not repeat this experience until at least six to eight quarters have elapsed. □

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