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Project Summary

High Temperature Dilute Acid Hydrolysis of Waste Cellulose: Batch and Continuous Processes

Walter Brenner and Barry Rugg

The full report describes a 5-year investigation on the conversion of cellulosic materials and wastes to glucose, potentially an enormous source of ethanol and a wide range of petrochemicals. Employing a co-rotating twin-screw extruder as reaction vessel, the process achieves a fully continuous dilute-acid hydrolysis at temperatures around 240°C and residence times of 5 to 10 seconds. It handles feedstocks ranging from waste paper pulp at 10% solids to corn bran to dry hardwood sawdust at 95% solids without pretreatment and gives good conversion yields, around 60% of the available cellulose, with low energy consumption.

Using a feasibility study based on accurately measured material and energy balances, economically attractive projections are given for scale-up from the 2 ton per day pilot plant, which has operated for three years, to a full-scale commercial plant producing 25 million gallons of ethanol per year.

Also given is a description of work on separation of the product, analytical techniques, studies on fermentation and bioconversion to methane and utilization of the hemicellulose and lignin fractions of the plant material. Environmental considerations are discussed, as well as a proposal for a mobile version.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The potential quantities of chemical feedstocks that could be obtained from waste cellulose are substantial. Assuming a realistic 12% available cellulose in the wastes and only 16% conversion to ethylene, the estimated 1550 million tons of farm waste alone would yield more than 30 million tons of ethylene annually—twice the U.S. consumption of this basic chemical building block in 1978. The economic feasibility of using waste cellulose depends greatly, of course, on both waste collection and processing conversion costs, as well as on the quantities and values of the various end products obtained.

Acid hydrolysis of cellulose has been extensively studied, particularly in connection with manufacturing ethanol from wood wastes. The discovery that cellulose can be hydrolyzed in acid solutions and converted to its monomer, glucose, was first reported by Bracconnot in 1819. The reaction has been experimentally investigated ever since then, mostly on a strictly empirical basis, in order to develop a cost-effective process for producing sugar from wood wastes and other sources of waste cellulose.

While the acid hydrolysis of cellulose is heterogeneous, it can be regarded as a homogeneous reaction provided that the cellulose reactant is dispersed in the form of fine particles, e.g., 200 mesh or less.

A very extensive amount of research and development has been aimed at the development of cellulose pretreatments which are both technically effective and economically viable. The basic approach has been to reduce the crystallinity and disrupt the hydrogen bonding, thus rendering the cellulose more accessible to hydrolytic depolymerization reactions. This should make it possible to approach the predicted glucose yields more closely.

Employment of high energy ionizing radiation has been shown to be at least equally as effective as widely used grinding pretreatments when the cellulose is exposed to dosages on the order of 100 megarads. Sugar yields as high as 70% based on the available cellulose content have been reported. Such large dosages of ionizing radiation are, however, too high for industrial usage. Thermal and radiation treatments have been combined to allow lower radiation dosage levels, which are more acceptable economically. Various chemical treatments have been investigated as well, with relatively little success.

Development of lower cost pretreatment technology, such as would produce substantial crystallinity reductions for improving the accessibility of cellulose, is recognized as a prime consideration for an economically as well as technically effective waste cellulose to glucose conversion process. This pretreatment must furthermore be combined with a high productivity, high yield acid hydrolysis process so as to optimize the conversion of the pretreated waste cellulose to glucose.

Experiments carried out at New York University's (NYU) laboratories have resulted in the development of a new high temperature acid hydrolysis process that overcomes the major problems that have been associated with this reaction. The important features of this process include the development of a cost-effective pretreatment for the waste cellulose that enhances its reactivity in an acid medium, and the establishment of reaction conditions that can produce yields on the order of 60% (based on the available cellulose values) in very short periods of time. Dilute sulfuric acid was used in the aqueous hydrolysis medium.

This rapid high temperature acid hydrolysis process has been successfully scaled up, first to a 1-liter and then to a 5-liter stirred autoclave reactor. The larger reactor and associated equipment were operated on a batch basis very satisfactorily for prolonged periods, and the glucose yields obtained were reproducibly consistent. Designing a continuous 1-ton/day waste-cellulose-to-glucose pilot plant facility was the next logical step using a screw-type conveyor, mixer, and reactor device for hydrolyzing waste cellulose in a slurry form.

A three-year program was implemented by an EPA Cooperative Agreement No. EPA-R-805239-030 with NYU. Activities were concentrated on the design of the 1-ton/day pilot plant unit, the necessary detailed specification of equipment and materials, their procurement, preparatory work necessary for equipment installation and equipment shakedown.

Two main types of feedstock were hydrolyzed, namely used newspaper and sawdust. The effects of pertinent reaction variables on the glucose yield obtainable from these wastes were studied. Separation of the glucose from unconverted material and other reaction products was also investigated. Exploratory studies were conducted on the acid hydrolysis of alternative waste cellulose sources, especially agricultural residues. The results of these investigations are the subject of the full report. This work was carried out at the Antonio Ferri Laboratories of NYU in Westbury, Long Island.

Description of Study

In the reactor itself, the following aspects of operation were addressed:

- feeding of cellulosic waste into high pressure reaction zone,
- precise control of reaction pressure, temperature, and residence time,
- addition of acid catalyst,
- addition of high pressure steam,
- minimization of moisture content passing through the reaction zone, and
- discharge of product from the high pressure reaction zone.

A vessel was designed and constructed for collecting and sampling the product as it flashed from the reactor, and thus a continuous conversion system that could hydrolyze paper pulp was accomplished.

In addition to reactor design, the problems of product (glucose) separation from the reaction mass as well as its analysis were studied using on-site analytical capability including semi-continuous centrifugation with the aim of obtaining additional information on separation efficiency.

By the onset of the third year, sawdust had been successfully hydrolyzed. This was seen as a major advance, since the ability to handle a low-moisture cellulosic feedstock without first forming a slurry meant that the level of water carried with the reaction mass was significantly decreased, and thus the energy requirement was reduced substantially. Sawdust as a feedstock naturally required redesign of the feeding section of the process. Also, the product was a more complex mixture of sugars requiring improved analytical capabilities.

Work during the final year of this study was aimed at improving the versatility, reliability, and efficiency of the extruder system. Bacterial fermentation studies were carried out at Louisiana State University for conversion of glucose to methane; yeast fermentation studies were commenced at NYU for conversion of glucose to ethanol. Materials and energy balances were developed and used as a basis for economic analyses and projections, and environmental impacts were studied.

Methods and Results

Several pretreatments for wastepaper prior to hydrolysis were evaluated. These included: (1) Wiley Mill grinding, (2) industrial grinding, (3) hydropulping (laboratory simulation), (4) electron beam irradiation, and (5) hydrogen peroxide degradation. A description of the procedures follows:

Wiley Mill Grinding: Newspapers were hand torn into 2" rectangles, then fed into a standard #3 laboratory size Wiley Mill fitted with a welded brass screen plate with ⅛" round perforations. The paper was passed through the machine once and separated according to pore size.

Industrial Grinding: Newsprint was passed once through a standard industrial Williams Hammer Mill Shredder, equipped with a ⅛" round hole perforated screen plate.

Hydropulping: Fifty gram samples of paper were weighed out and hand torn into one-gallon Waring Blender with 2450 gms of water to make a slurry of approximately 2% solids. The blender was run at high speed for 15 seconds. The excess water was then filtered off with a Buchner funnel to make a higher solids slurry prior to hydrolysis.

Irradiation: Fifty gram samples of paper were hydropulped and filtered to a preset slurry concentration, then sealed in plastic bags. These samples were exposed to high energy electrons at a specified dosage (10 and 20 megarads).

Hydrogen Peroxide: Fifty gram samples of paper were hydropulped with 2450

gms of 0.1 M acetate buffer (pH - 4.2) containing 2.31 gm $FeSO_4$. The slurry was secured in a plastic bucket and equilibrated in a 30°C water bath. Then 82.5 gm of 30% H_2O_2 was added and the reaction begun with constant agitation. The runs were 16-18 hrs in duration, after which the peroxide was dissipated and the treated newspaper was filtered, washed, and refiltered before being subjected to acid hydrolysis.

Hydrolysis batch experiments were initially run in a 1-liter reactor and in due course scaled up to a 5-liter reactor. These reactors were both stainless steel, stirred autoclaves which were instrumented for reading temperatures and pressures. Acid solutions were injected from an external bomb after the reaction mass was heated to the appropriate temperature. The reactors were fitted with quick-acting discharge valves and properly-sized collection vessels. In the early experiments using the 1-liter reactor, a known amount of ice was put in the collection vessel to quench the reaction. With scale-up to the 5-liter reactor, a 55-gallon drum was adapted with baffles to absorb the thermal and kinetic shock of the discharge. In this case, flashing to atmospheric pressure was sufficient to quench the reaction, thus dilution of the product with ice was eliminated.

A typical procedure was as follows: the waste cellulose slurry, approximately 10% solids, was poured into the autoclave, a typical charge being 1000 gm for the 1-liter reactor and 3000 gm for the 5-liter reactor. The autoclave was then electrically heated with stirring to various reaction temperatures, with 220-240°C found most desirable for optimum glucose conversions. The pressures required to obtain these temperatures were in excess of 500 psi. When the cellulose slurry reached the desired temperature, a predetermined quantity of acid was injected into the autoclave. This was accomplished using the inert gas from the nitrogen cylinder as the pressure medium to force the acid into the autoclave. The acid hydrolysis reaction was then run with continuing autoclave agitation for predetermined reaction periods, ranging from 5 seconds to more than 2 minutes. After reaction, the "quick release" ball valve was opened and the contents of the reactor were discharged rapidly so as to minimize hydrolytic degradation reactions of the glucose formed. The reaction mass was filtered to separate the glucose in the liquor for subsequent analysis.

Specific experimental data of typical acid hydrolysis runs which were carried out at 232°C in the autoclave shows the glucose yields as a function of reaction time for a range of acid strengths, e.g., 0.58% to 2.24%. The 232°C temperature was employed for all the hydrolysis experiments because the results of previous experimental work had shown it to be optimal for glucose yield. The majority of the acid hydrolysis experiments were carried out with Eiley milled newspapers as the waste cellulosic feedstock in order to ascertain maximum glucose yields with an "accessible" feed as a function of acid content at 232°C hydrolysis temperature. These experiments established the range of acid content which gave the highest glucose yields and the reaction times necessary to achieve them. Experiments with hydropulped cellulose feedstock were then run at three acid concentrations, 0.87%, 1.29%, and 2.24% with glucose yields realized comparable with those obtained from Wiley milled material.

Conclusions

Maximum glucose yields increase with acid content while the reaction times necessary to achieve them decrease; the experiments carried out show that glucose yields on the order of 35% and higher can be obtained with acid strengths in the range of 1.30% to 2.25%. Reaction times for maximum glucose yields are 20 seconds or less at the preferred range of acid concentrations.

Hydropulped waste newspapers give glucose yields which approach rather closely those obtained from the more expensive Wiley milled paper; also, reaction times are similar. Thus, glucose conversions on the order of 35% can be obtained in less than 20 seconds at the preferred range of acid concentrations, with cellulose concentrations of 10% in the slurries.

Once it was shown that the rapid dilute acid hydrolysis concept could be scaled up through the NYU 1-liter and 5-liter batch reactors, serious consideration was given to devising a method for making the process continuous, and scaling up further to a pilot plant, and ultimately industrial scale. Requirements are that a reaction vessel must be charged with feedstock and brought to the conditions of temperature, pressure, and acid content, then discharged within the few seconds required for optimum conversion.

Summary

The principal result of this study was the successful development of a fully continuous dilute acid hydrolysis process for converting cellulose to glucose. Batch hydrolysis studies carried out for two years gave extensive data on which the continuous process was based.

Pretreatment studies led to the belief that to gain cellulose accessibility, one needed to impart energy in some form to the cellulose. A combination treatment of high energy electron beam irradiation in conjunction with hydropulping was seen to be more effective while less costly than mechanical treatments. Results of chemical pretreatments were inconclusive. Hydrolysis experiments made with organic acids in place of sulfuric acid to reduce corrosion proved effective, but too expensive for serious commercial consideration. The emphasis on pretreatments diminished as development of the continuous reactor proceeded.

Based on plant trials, a decision to use a commercially available co-rotating twin-screw extruder was made because of its modular design and inherent versatility. The problem of forming a high pressure reaction zone in a flow system was the key issue. This involved creating an upstream seal while material is fed in, and a downstream seal while material is discharged.

The feasibility of continuously hydrolyzing various cellulosic feeds at high glucose yields using the extrusion technique was proven. Additionally, the capability of handling high solids feeds resulting in a product with high glucose content was established for the extruder.

The studies on process development branched out to issues of handling the product once out of the reactor. These issues included separation, fermentation, and analysis; further subjects included environmental impact and overall process economics.

Trial separation studies were done using a semi-continuous centrifuge. It was soon evident that hydrolysis reaction conditions played an important role in product separability. If the cellulose were "under-reacted," the product contained a high fiber content and subsequently the water-soluble fraction was difficult to remove. At best, a filter cake with 30% solids was produced in the centrifuge. Further washing of the cake to extract residual sugars caused excessive dilution. However, under more severe reaction conditions where more of the fiber properties of the cellulose were destroyed, it was shown that the product could be separated more effectively and centrifuge cakes of 50-70% solids content could be produced.

Fermentation studies on the glucose initially concentrated on the generation of methane. Subsequent studies on yeast fermentation of the glucose to ethanol, using a gradual acclimation technique, were successful.

High pressure liquid chromatography was the method used for separating and analyzing carbohydrate mixtures including monosaccharides, oligosaccharides, and breakdown products allowing detailed evaluation of the efficiency of the process.

Environmental studies indicate no significant adverse impact. Conventional water and air treatments are adequate. Economic analyses and a full engineering feasibility study have been carried out for the production of fuel grade ethanol for gasohol from glucose, and indications are that such a process would be competitive with ethanol from grain under current market conditions.

Walter Brenner and Barry Rugg are with New York University, Department of Applied Sciences, New York, NY 10003.
***Charles Rogers** is the EPA Project Officer (see below).*
The complete report, entitled "High Temperature Dilute Acid Hydrolysis of Waste Cellulose: Batch and Continuous Processes," (Order No. PB 86-143 484/AS; Cost: $16.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
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