Aqueous Extraction of Sugarcane Bagasse Hemicellulose and Production of Xylose Syrup

M. Saska* and E. Ozer
Sugar Station/Audubon Sugar Institute, Louisiana State University Agricultural Center, Louisiana Agricultural Experiment Station, Baton Rouge, Louisiana 70803

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At the optimum level of severity, the aqueous extraction of sugarcane bagasse, an abundant agricultural residue, gave, depending on the degree of comminution, 60% to 89% yield of xylose, most of it in the form of a water soluble xylan. A process for producing xylose-rich syrups was conceived and tested, consisting of aqueous extraction, acid hydrolysis of the concentrated aqueous extract, centrifugal clarification of the hydrolysate, and recovery of the acid by continuous ion exclusion. The cost estimate indicates operating costs on the order of $0.12 to $0.15/kg xylose, in the form of xylose-rich molasses.
Key words: biomass utilization • hemicellulose hydrolysis • sugar–acid separation

INTRODUCTION

Among the several potential biomass sources, sugarcane bagasse has frequently been mentioned in the literature as one of the most promising for the biomass-to-sugars process, for fuel grade ethanol, or other uses. It was estimated[12] that without resorting to supplemental fuels, the existing sugarcane mills could free up 35% to 45% of the total bagasse produced for alternate uses if sufficient economic incentives were in place. The frequently used estimate of $30 to $40/ton (dry) for bagasse at the mill site, with zero transportation cost, which is based on its fuel replacement value, is too high for approximately a first 10% (or 0.5 million tons annually in U.S.; Table I) that can be diverted to other uses without any significant investments on the part of the sugar producers. The net cost of the next 25% to 35% of the total bagasse production (1.1 to 1.6 million tons per year) will depend on the cost of the high efficiency boilers, vapor recompression units, etc., that will be needed to bring about the required energy savings, but should still be below the fuel replacement value. Only if even more bagasse is required for alternate uses, the $30 to $40/ton (dry) estimate will apply.

The preferred conversion process[2,17] involves prehydrolysis with 0.5% to 1.0% dilute sulphuric acid at 100° to 130°C to solubilize most of the hemicellulose, which is then converted by xylose-fermenting microorganisms to other products. At the same time, cellulose, swollen and decrystallized to some degree, is made accessible to hydrolysis with enzymes or strong acids. Simultaneous enzymatic saccharification and fermentation (SSF) is the most promising of processes for conversion of the pretreated cellulose to ethanol. Based on the conditions of Bernhardt and Proudfoot,[2] the cost of the chemicals involved in the pretreatment; that is, sulphuric acid and lime to neutralize the liquor and gypsum disposal amounts to $0.010/kg bagasse (dry) or $0.050/kg xylose. Although the required amount of sulphuric acid is relatively small, its recovery would be desirable if it could be done economically. This does not appear feasible from the dilute hydrolysates generated in this process. Furthermore, concentration of the acidic hydrolysates with 2% to 4% sugars and 0.5% to 1% sulphuric acid to at least 10% sugars for efficient fermentation would be expensive because of the severe corrosion problems with common construction materials. An alternative is steam/aqueous pretreatment, either in a high pressure steam-explosion equipment, or in more conventional lower pressure continuous or batch digesters. The latter was used in this work. Because not all extracted hemicelluloses are hydrolyzed to sugars in the steam/aqueous pretreatment at the optimum severities for hemicellulose extraction, postextraction hydrolysis with sulphuric acid of the concentrated extracts was investigated. The recovery of sulphuric acid from the low volume, concentrated hydrolysates becomes then feasible. Separation of the acid by ion exclusion chromatography on strong cation exchangers appears most promising, and has been tested previously on single column[4] and continuous multicolumn systems (Advanced Separation Technologies, Inc., Lakeland, FL). An eight-column simulated moving bed pilot unit was used here to optimize the recovery of sulphuric acid from the concentrated pretreatment hydrolysates. Of even more interest than in the bagasse pretreatment, where the acid consumption is modest, is the recovery of sulphuric acid from the glucose liquors from the concentrated acid hydrolysis of cellulose, where the acid recycle is a precondition for economic viability.[4] The acid–sugar separation optimized here for concentrated pretreatment liquors is also directly applicable for the cellulose hydrolysates, with the exception of the construction materials that will have to be designed such as to withstand the highly corrosive hydrolysates with 20% or so of sulphuric acid.

The enzymatic or acid digestibility of pretreated cellulose

* To whom all correspondence should be addressed.

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Table I. Estimated U.S. bagasse production, in million tons (dry) per annum.

	1991	1992	1993
Florida	2.4	2.3	2.3
Louisiana	1.0	1.2	1.2
Hawaii	0.9	0.8	0.8
Texas	0.1	0.2	0.2
Total U.S.	4.4	4.5	4.5

was not investigated here, but is expected to be comparable to the steam exploded bagasse at comparable severities as used in this work.

MATERIALS AND METHODS

Aqueous Extraction of Sugarcane Bagasse

A 20-L Monel batch digester (Fig. 1) was used for the bagasse extraction. In most cases, the digester was charged with 1 kg of whole sugarcane bagasse from a nearby Louisiana sugar mill (Table II) and an amount of water such as to obtain the desired (dry) solid–liquid ratio, where the liquid is the water added and the one in the raw material. The ratios 1:5 and 1:10 were used, the former is close to the minimum amount of liquid that will still allow a sufficient degree of agitation in this type of reactor. Naturally, reducing the amount of water used for extraction will lead to considerable savings later in recovering the extracted sugars. In some experiments, the raw bagasse was passed once

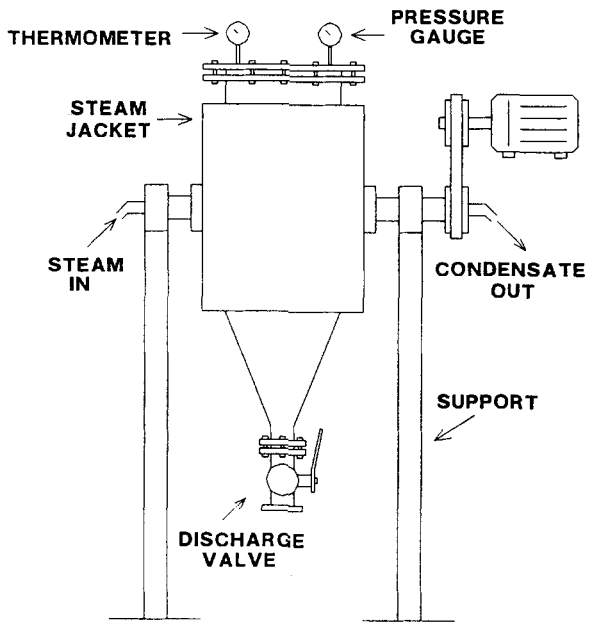

Figure 1. The 20-L Monel digester used for extraction of sugarcane bagasse. The jacket of the reactor was heated with steam and rotated at circa 0.3 rpm around its axis.

Table II. Average composition of the Louisiana sugar cane bagasse used for the aqueous and dilute acid extractions, in weight percent (dry basis).

Glucan	39.1
Xylan	18.0
Galactan	1.4
Arabinan	2.4
Mannan	0.5
Klason lignin	22.6
Acid-soluble lignin	1.9
Thermogravimetric ash	4.4
Total	90.3

through a Bauer disk mill, giving finer fibrous particles of around 0.2 × 8 mm size, and extracted as before.

After the reactor was charged and closed, steam was released to the jacket of the reactor, and counting of the processing time was started when the temperature inside nearly reached the final temperature. This in most cases took between 15 and 30 min.

During the extraction, the reactor was rotated at about 0.3 rpm. When the desired processing time (and treatment severity) was reached, steam supply was turned off and the liquid discharged through a screen from the bottom of the reactor. Solid residues were recovered after cooling and opening the reactor. The amount of water evaporated during discharging of the (hot) reactor was calculated from the water balance. The processed bagasse sample was washed with deionized water, and in some cases dewatered with a hydraulic press. All samples were kept frozen in closed containers until further analysis.

Dissolved solid content of the liquid samples was measured by refractometry, their turbidity in NTU with a Hach ratio turbiditimeter, and the moisture content in the solid samples was determined by drying at 95°C for 150 min with an infrared moisture analyzer. As the extraction of pentosans (xylans) was the main focus of this work, each extract was analyzed in detail for its content of free xylose, total pentosans, and pentosans water soluble at ambient temperature.

The total xylan content in the extract was obtained from the differences in xylose concentrations determined in the raw extract and extract subjected to complete hydrolysis with 6.5% w/w H_2SO_4 for 2 h at 100°C. The content of the soluble xylan was determined from xylose concentrations in an extract first clarified by filtration with a 4.5-μm cellulose acetate disk, before and after complete hydrolysis. The insoluble xylan was then obtained as the difference between the two. Since no free xylose is expected to be present in the original bagasse, the xylose content of the raw extracts is assumed to correspond to the xylan autohydrolyzed during extraction.

The monosaccharides in the raw and hydrolyzed extracts were determined with HPLC, using either an anion exchange CarboPac PA1 column (Dionex) and a PED (pulsed electrochemical) detector, or a cation exchange sugar column (Bio-Rad HPX-87K) and an RI detector.

In addition, carbohydrate and lignin analyses of the solid

samples, and in some cases of the extracts as well, were done at the Biobased Materials Center and the Department of Wood Science and Forest Products at Virginia Polytechnic Institute, using a slightly modified version of the summative analysis procedure outlined previously.[5,6] Solid samples were milled to a 40-mesh size or less with a Wiley mill, and dried over P_2O_5. Samples of 0.1 g (dry weight) were taken and placed in 50-mL glass autoclave bombs, combined with 1.0 mL 72% H_2SO_4, and incubated in a 30°C water bath for 1 h with occasional stirring. After incubation, 30 mL distilled deionized water was added to each sample bomb, sealed, and autoclaved at 120°C for 1 h. After cooling, the acid-insoluble (Klason) lignin was filtered out, and determined by drying at 105°C.

To account for the loss of one water molecule on formation of a glycosidic bond in the polysaccharides, the contents in the original material of the polysaccharides were calculated from the concentrations of the monomers determined with HPLC using factors 0.90 and 0.88 for glucan and xylan, respectively, with the amount of glucan converted in the analytical extraction to hydroxymethylfurfural (HMF) using a factor of 1.3, and the amount of xylan degraded to 2-furfural using a factor 1.4.[5]

The diluted filtrate was analyzed for its content of acid-soluble lignin by measuring its absorbance at 205 nm.[6] The sugars, glucose, fructose, xylose, galactose, arabinose, and mannose and their acid degradation products, HMF and 2-furfural (2-F), were determined with HPLC equipped with cation exchange columns (a Bio-Rad HPX-87P for sugars and a Brownlee Labs PPH-GU guard column for HMF and 2-F) with RI (sugar) and UV (277 nm, furfurals) detection.[5] Ash was determined by thermogravimetry at 800°C at 10°C/min under an air purge.

For comparison, a few tests were done on extraction at conditions identical to those suggested as "optimum" for dilute acid pretreatment[2]: 0.7% H_2SO_4 (concentration calculated including the bagasse moisture); and solid (bone dry):liquid ratio 1:5, at 132°C for 75 min.

RESULTS

Raw bagasse contained on average 39.1% glucan, most of course in the form of cellulose, although an amount comparable with that of arabinose[2] may be a part of the hemicellulose complex. The cellulose content found here agrees well with the 38% reported from South Africa and 36.8% from Louisiana.[9] The total content of hemicellulose, a xylose-based polysaccharide[3,7] with some glucose, arabinose, galactose, and mannose, and assuming that 2.4% glucan came from hemicellulose instead of cellulose, and disregarding the minor contribution to hemicellulose from the acetyl, glucuronil, and methyl groups (that split off on hydrolysis) is 24.7%, somewhat lower than reported for Louisiana bagasse but within the wide range of 20% to 33% tabulated for a number of cane varieties and geographical conditions.[9] No fructose was detected in any of the samples.

Raw aqueous extracts (Table III) were turbid, cloudy green-yellowish liquids, darker at higher severities, with 2.5% to 3.5% dry solids, slightly acidic (pH 4 to 4.5) on account of acetic acid released from hemicellulose during hydrolysis, with the sugar purity (percent of dry solids) close to 50%. Xylose was the main component, and to a large degree still present as xylose-based oligo- and polysaccharides as indicated in more detail in Figure 2. HFH and 2-F determined in the extracts using the summative analysis of Kaar[5] as roughly 0.5% (dry basis) were again assumed to be the artifact of the analysis and were added, using the factors given earlier to glucose and xylose, respectively. Although some were certainly generated during extraction, these were likely to be volatilized at least to some degree during discharge of the superheated contents after heating. Furthermore, their contents found in extracts were comparable with those in the original bagasse, where no HMF and 2-F was expected.

The effects of time and temperature on the extent of solubilization of carbohydrates were combined in a single severity factor, R,

$$R = t * e^{(T-100)/14.75}$$

with residence time t in minutes, and temperature T in degrees Celsius as suggested earlier.[8] The extraction temperature ranged between 150° and 170°C (steam pressure between 0.68 and 1.01 MPa or 100 to 150 psig), so that the variations of log R in Figure 2 reflect variations in both time and temperature. Although the severity factor equation, based on the assumed equivalence of time and temperature effects, appears to hold reasonably well, there is some indication that higher temperature/shorter time conditions give somewhat better yields than lower temperature/longer time combinations. Overall, hemicellulose extraction (reported as xylose in Fig. 2a and b) peaked at a severity 3.9 for both ground and "as-is" bagasse. For ground bagasse (Fig. 2b), at log R of 3.9, a total of 14 g xylose or 89% of

Table III. Representative extract composition (as monosaccharides) from aqueous and dilute acid extractions of "as-is" bagasse.

	Aqueous	Dilute acid
pH	3.9	2.0
Dissolved solids	2.8	7.4
Sulphur	0.2	2.7
Xylose	43.4	35.9
Glucose	1.0	9.7
Galactose	2.0	1.0
Arabinose	4.2	1.9
Mannose	0.0	NA
Klason lignin	8.9	NA
Acid-soluble lignin	11.8	NA
Thermogravimetric ash	33.5	NA
Total	104.8	48.5

Data expressed in percentage of dry solids, except dissolved solids (from RI) which are in grams/100 g solution. Solid:liquid ratio = 1:5 log R = 4.0 (aqueous extraction). NA = not analyzed.

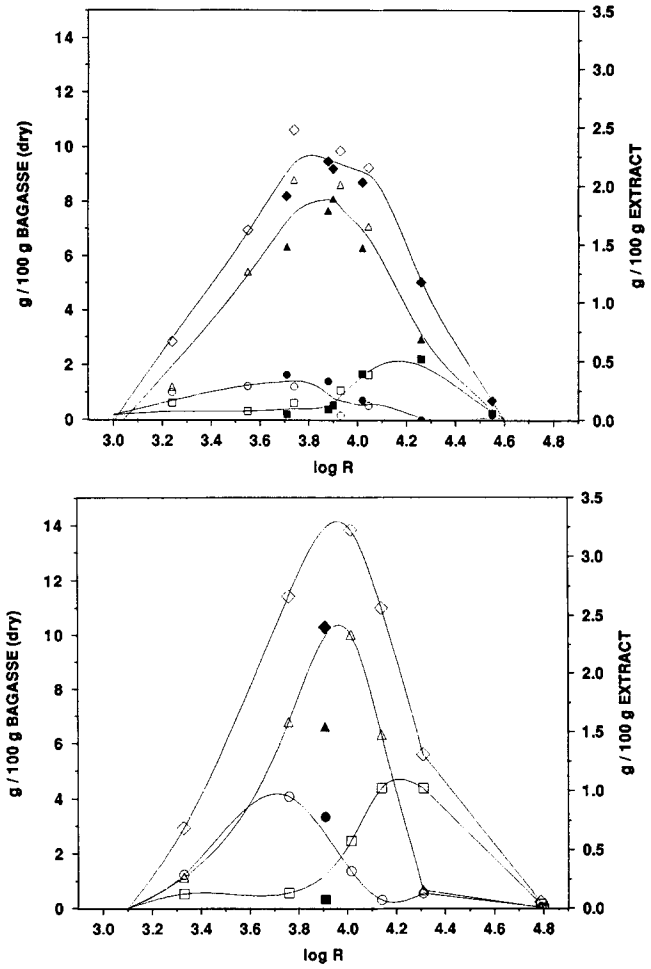

Figure 2. Recovered amounts and extract composition at various severities of aqueous bagasse extracts: (a) "as-is" bagasse; and (b) ground bagasse. Solid symbols: pressure ca. 100 psig, 155°C; empty symbols: pressure 130 to 150 psig, 160° to 170°C. (○) Insoluble xylan (reported as xylose); (△) soluble xylan (as xylose); (□) free xylose; (◇) total recovered xylose.

the original amount was recovered in the extract per 100 g dry bagasse. Of the recovered total, 9% was in the form of an insoluable xylan, 74% as water soluble xylan, and 17% as free xylose. With "as-is" bagasse (Fig. 2a), the recovery was about 60%, considerably lower than with finely ground bagasse, with about the same ratios of the soluble xylan, insoluble xylan, and free xylose.

The recovery of the water-insoluble fraction was favored at lower severities (3.7), although at these conditions most of the extracted xylan has already been solubilized but not yet completely hydrolyzed. The term "water soluble" refers here to ambient temperature, and it does not necessarily imply that this fraction was not solubilized at the extraction conditions. In the absence of more detailed structural analysis, it is assumed that it refers to that part of xylan that more or less depolymerized during the extraction, rather than to a structurally different oligo- or polysaccharide. As the severity of the treatment increased, the yields of insoluble and soluble xylan fractions became lower and nearly zero at log R of 4.3. The sugar yield became practically zero at log R of 4.8. No xylan/xylose extraction is expected below severities of 3.2. The data in Figure 2a and b represent experiments with both 1:5 and 1:10 solid:liquid ratios. No significant difference in the sugar yield was found between the two data sets.

The residual bagasse (Table IV) still contained a substantial amount of unsolubilized xylan, corresponding perhaps to the fraction of bagasse hemicellulose reported earlier to form between 23% and 39% of the total that is extractable from bagasse with diluted acids at a distinctly slower rate than the first fraction.[6] Two tests performed here with dilute H_2SO_4 hydrolysis confirmed the higher degree of hemicellulose extraction; that is, lower residual concentration in extracted bagasse at extraction conditions recommended by Bernhardt and Proudfoot,[2] but not necessarily higher recovery in the liquor because of faster xylose degradation at higher acidities.[13]

Dilute Acid Hydrolysis of Aqueous Extracts

At the conditions found optimum here for the solubilization of hemicellulose, 80% of the extracted xylose was still in the oligo- or polysaccharide form, and unless these are the target compounds, postextraction hydrolysis is necessary prior to fermentation or xylose recovery. Both dilute acid and enzymatic hydrolyses are feasible, although the latter may be complicated by the heterogeneity of the xylans. Dilute H_2SO_4 was chosen here, primarily because of its low cost and a possibility of near complete recovery from the hydrolyzed extracts.

To reduce the extract volume and reduce the acid consumption, the raw extracts were first concentrated under vacuum to 20% to 40% dry solids. Preliminary experiments showed that the rate of hydrolysis depended only on temperature and acid concentration (mass 98% H_2SO_4 per unit mass of the concentrated extract), but not on the extract concentration up to about 30% dry solids. There was some indication though that conversion became lower at extract

Table IV. Representative composition of the residual bagasse, after aqueous and acid extractions of "as-is" bagasse.

	Aqueous	Dilute acid
Sulphur	0.2	1.1
Glucan	50.1	53.3
Xylan	7.6	1.3
Galactan	0.3	0.0
Arabinan	0.0	0.3
Mannan	0.0	0.0
Klason lignin	30.7	35.0
Acid-soluble lignin	1.2	1.3
Thermogravimetric ash	NA	NA
Total	89.9	91.2

The same extraction conditions as in Table III. All data expressed in percent dry solids. NA = not analyzed.

concentrations of the order of 40%. Furthermore, during the hydrolysis, additional fine and bulky acid-insoluble lignin precipitated, and the high concentration slurries were difficult to handle. A concentration of 25% dry solids was therefore chosen as a compromise between minimizing the acid use (t H_2SO_4/t xylose) and ease of clarification of the hydrolyzed slurries. Near 100% hydrolysis was achieved within 30 to 90 min, depending on the acid concentration and temperature (Fig. 3), although some care must be taken because of rapid xylose degradation above 100°C. The lignin precipitated in the hydrolysis tended to cake and settle on the walls and bottom of the reactor. Addition of 1% to 1.5% (w/w) of fine extracted bagasse to the reactor at the beginning of the hydrolysis was found sufficient to prevent caking.

Acid consumption (98% H_2SO_4) in the hydrolysis was between 0.8 (conditions 1 in Fig. 3) and 0.2 kg (conditions 3) per 1 kg xylose produced, or \$0.064 to \$0.016. The lignin in the hot hydrolyzed extracts was in the form of fine suspension, in part probably bound to the fine bagasse particles added to the reactor to prevent caking. More lignin precipitated as the solution cooled. Any physical clarification (filtration or centrifugation) must therefore be done at low temperature. Preliminary laboratory trials with pressure filtration at room temperature gave very low fluxes, of the order of 30 to 100 L/m^2 per hour, and because of cake compressibility, nearly independent of the pressure in the range 20 to 60 psi. Centrifugation after cooling to ambient temperature with laboratory batch and continuous solid bowl centrifuges at 2000 to 3000g gave clear solutions with turbidities between 50 and 250 NTU (at 25% dry solids). The extracts (Table V) clarified in this way were stable (no turbidity developed) and suitable for xylose recovery.

Increase in glucose content compared to the raw extracts (Table III) prior to hydrolysis was probably from cellulose hydrolysis of fine bagasse particles that passed through the screen and the 1% ground pretreated bagasse added to the hydrolysis reactor to prevent caking of the lignin precipitate. Sixty to 70% of the lignin in the raw extract was removed in the clarification, and recovered as a solid cake in a 3:1 mixture with fine bagasse, at a rate of 0.05 kg lignin (dry) per 1 kg bagasse (dry) extracted.

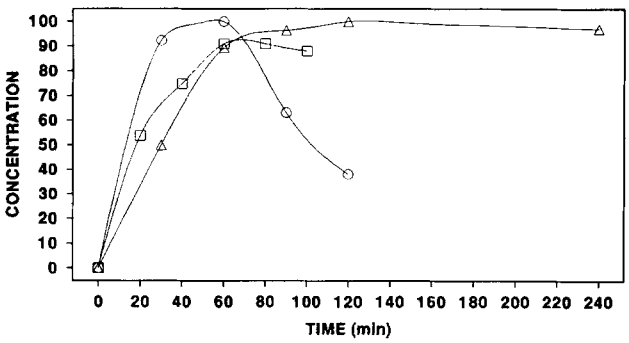

Figure 3. Relative xylose concentration in solution at three hydrolysis conditions: (△) 100°C (atm. pressure), 7.0 g of H_2SO_4/100 g 26% DS concentrated aqueous extract; (□) 100°C, 4.2 g H_2SO_4/100 g; (○) 130°C, 1.5 g H_2SO_4/100 g. Calculated as 100 $(C_x - C_{x,in})/(C_{x,max} - C_{x,in})$— where C_x is the xylose concentration in solution (g/L); $-C_{x,in}$, the same prior to hydrolysis; and $C_{x,max}$, the xylose concentration in the solution hydrolyzed at 100°C, 7.0 g H_2SO_4/100 g conc. aq. extract, and 120 min.

Table V. Representative composition of the clarified hydrolysate, excluding sulphuric acid, in grams per 100 g non-H_2SO_4 solids.

Xylose	45.9
Glucose	5.6
Galactose	1.8
Arabinose	4.0
Mannose	0.0
Klason lignin	1.8
Acid-soluble lignin	7.4
Thermogravimetric ash	NA
Total	66.5

The same extraction conditions as in Table III. NA = not analyzed.

Recovery of H_2SO_4 From Hydrolyzed Extracts

A simulated moving bed (SMB) adsorber with eight columns, packed with Dowex Monosphere 99 chromatographic resin (320-μm particle size) in H^+ form, was used to partially optimize the H_2SO_4 sugar separation. Detailed description of the installation, procedures, and fundamentals of the SMB operation can be found in our previous publications[14,15] and general literature on industrial chromatography separations.[18] All columns in an SMB system such as the one in Figure 4 are connected in series. Periodically, all the inlet (water, feed, and internal recycle) and outlet (sugar and acid) products are switched downstream. This simulates a semicontinuous motion of the resin relative to the ports and achieves the advantages of a countercurrent operation.

Preliminary experiments with batch separation on single 1-m columns, packed with the identical resin as the SMB system, indicated no separation (identical chromatographic

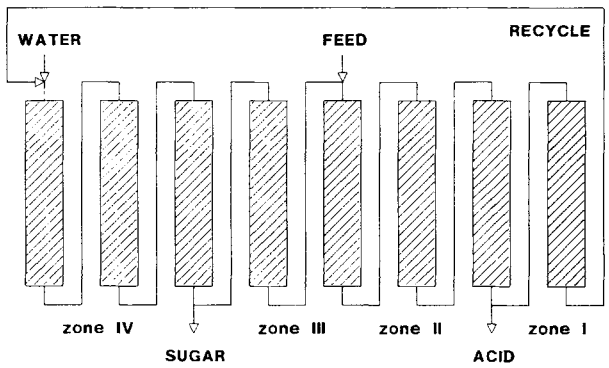

Figure 4. Schematics of the eight-column, pilot simulated moving bed (SMB) adsorber. The flow direction in all in-series connected columns is downward, the arrows indicate the inlet (water, internal recycle, and feed) and outlet (sugar product and acid product) ports. The periodic switching of all ports downstream simulates the countercurrent motion of the resin.

behavior) between glucose and xylose on the H^+ form of the resin. Ten SMB tests, each lasting between 10 and 20 h were done, two with hydrolyzed extracts, the rest with synthetic sulphuric acid–glucose mixtures, with xylose added in smaller quantities in some tests to further verify that the two sugars behaved identically. The feed for the SMB trials characteristically consisted of 4% H_2SO_4 and 16% sugar, corresponding roughly to an extract hydrolyzed with 4 kg H_2SO_4 per 100 kg of the 25% dry solids extract.

The operational parameters and performance are summarized in Tables VI and VII. The sugar product was only slightly diluted with 15% dry solids, of nearly 100% purity (almost no acid present), containing 94% of the sugar present in the feed. The remaining 4% went into the acid product, which was more dilute with 2% dry solids, 95% acid recovery, and 95% acid purity.

The acid product was concentrated under vacuum, and reused for hydrolysis of the crude extracts. The hydrolysis rate was found identical as in the case of hydrolysis with fresh H_2SO_4.

DISCUSSION

Principal elements of a process for steam pretreating of sugarcane bagasse in preparation for acid or enzymatic hydrolysis of cellulose, and production of a xylose-rich syrup for xylose, arabinose, or galactose production, are presented in Figure 5. Bagasse is pretreated, preferably in a screw-fed continuous digester (1) of the PANDIA type advocated for rapid pulping of nonwood plant fibrous materials.[1] The dilute aqueous extract is concentrated to 25% to 30% DS in the evaporator (2), and fully hydrolyzed with sulphuric acid in the reactor (3). Preferably, a small amount (1% of the weight of the concentrated extract) of ground raw or pretreated bagasse is added in the hydrolysis reactor to prevent caking of the acid-insoluble lignin precipitate. After cooling the hydrolysate–lignin suspension, it is clarified with a continuous decanting centrifuge (5). The clear delignified hydrolysate is further concentrated in the evaporator (2), and pumped into the eight-column continuous ion-exclusion separator where at least 95% of sulphuric acid is recovered and recirculated back into the hydrolysis reactor (3). Approximately 15% DS syrup composed of xylose and smaller quantities of glucose, arabinose, and galactose and other nonsugar impurities can then be fermented or purified and further separated into its individual sugar components with either a batch or preferably a continuous chromatography system analogous to the one used here for recovery of sulphuric acid. A simultaneous separation of three components, for example, xylose, glucose, and arabinose, is feasible with a modified simulated moving bed system.

Some aspects of the proposed process remain to be verified on a realistic pilot facility; they are: the efficiency of hemicellulose extraction with a continuous system, at the same severity but with less water then used in the present batch system; the enzymatic digestibility of the pretreated bagasse; and the purification and fractionation of the xylose syrups and combustion or other properties of the lignin fraction. On the other hand, the hydrolysis of the concentrated extracts, clarification of the hydrolysates, and the recovery of sulphuric acid from the sugar–acid mixtures can probably be scaled-up quite confidently based on the present results.

For a cost estimate, two scenarios were considered (Table VIII): (1) 15% DS xylose-rich syrup is produced, and all pretreated bagasse is returned to the boilers; and (2) pretreated bagasse is further hydrolyzed to glucose. Sixty percent and 90% hemicellulose conversion was considered as a basis for "as-is" and ground bagasse, while 80% and 90% cellulose conversion was assumed for the two respective cases. No byproduct credit was given for the lignin product. With the bagasse composition as in Table II, the sugar (monosaccharide) yields used for the calculations, in kilograms sugar produced/kilogram (dry) bagasse were, in the case of xylose syrup production, only 0.168 and 0.253 for

Table VI. Parameters of the acid–sugar SMB separation.

Feed (mL/min)	90
Water (mL/min)	234
Acid product (mL/min)	229
Sugar product (mL/min)	90
Recycle (mL/min)	214
Switch time (min)	8.4

Table VII. Purity and recovery of SMB products.

Sugar product		Acid product	
Recovery	Purity	Recovery	Purity
94%	100%	95%	95%

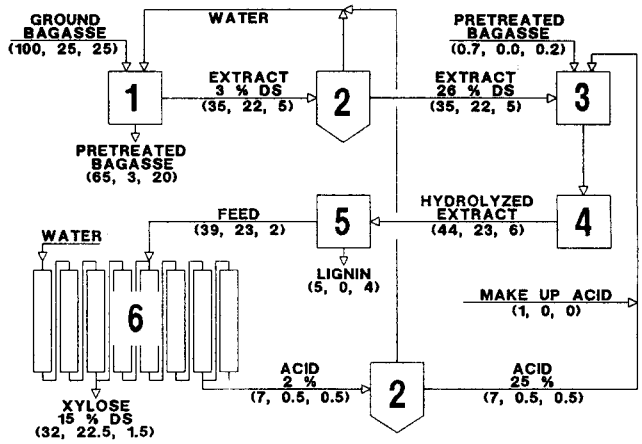

Figure 5. Schematics of a process for steam/aqueous pretreatment of ground sugarcane bagasse and production of 15% DS xylose-rich syrup, with continuous ion-exclusion recovery of sulphuric acid: 1 = hemicellulose extraction; 2 = multistage vacuum evaporation; 3 = xylan hydrolysis; 4 = cooling; 5 = centrifugal clarification: and 6 = continuous ion exclusion. The numbers (X, Y, Z) in parentheses indicate the approximate mass flows of the principal components: X, total solids; Y, hemicellulose components; and Z, lignin.

Table VIII. Estimated pretreatment costs, for production of 15% DS syrup of xylose (with minor amounts of glucose, arabinose, and galactose), including energy and chemical cost and byproduct credit, in $/kg sugar produced.

	Ground bagasse		Mill run bagasse	
	(1)	(2)	(1)	(2)
Raw material	0.119	0.048	0.179	0.061
Bagasse preparation[a]	0.020	0.008	0.000	0.000
Hemicellulose extraction[b]	0.040	0.016	0.060	0.020
Evaporation (extract and dilute H_2SO_4)[c]	0.022	0.009	0.034	0.011
Hydrolysis[d]	0.001	0.000	0.002	0.001
Clarification[e]	0.003	0.001	0.004	0.001
Acid recovery[f]	0.012	0.005	0.018	0.006
Byproducts credit[g]	−0.093	−0.022	−0.153	−0.034
Total	0.124	0.065	0.144	0.066

[a]0.10 kWh/kg bagasse (dry)[10]; $0.05/kWh.
[b]3.8 kg steam/kg bagasse (dry); steam $0.0045/kg.
[c]6.3 kg water/kg bagasse (dry), 1.3 kg steam/kg bagasse (dry).
[d]0.00075 kg H_2SO_4/kg conc. extract, H_2SO_4 at $0.08/kg.
[e]0.0025 kWh/kg conc. extract.
[f]95% acid recovery, cost of electricity and resin replacement.
[g]Same value as original bagasse at same moisture content.

"as-is" and ground bagasse, respectively; and, in the case of production of both xylose and glucose syrups, the latter by cellulose hydrolysis, 0.494 and 0.620, respectively. For a conservative estimate, the raw material cost was included at $0.03/kg (dry), although the true cost of the first 10% or so diverted from the boilers is expected to be close to zero, if the bagasse hydrolysis facility is operated at the mill site and jointly with the conventional sugarcane milling process. With the (fuel value) credit for the extraction residue, the raw material cost adds $0.026/kg sugar. Without this cost, the estimates range from $0.039 to $0.118/kg sugar. The former, assuming hydrolysis of both hemicellulose and cellulose, excludes the actual cost of cellulose hydrolysis, which at the anticipated use of 1.5 kg H_2SO_4/kg sugar and 95% acid recovery can be estimated at $0.006/kg sugar. For the acid recovery with ion exclusion[4] the resin replacement and evaporation costs were estimated at $0.04/kg sugar. This may be a conservative estimate considering that the actual water and resin use in the acid recovery process established in this work were lower than anticipated by Hartfield and Hester.[4]

In comparison with dilute acid extraction of hemicellulose, the aqueous process presents several advantages: lower corrosion conditions in the extraction and concentration equipment; less xylose degradation in extraction; and less degradation byproducts in the extracts and pretreated bagasse. In cases in which the pretreated bagasse is to be sent back to the boilers for steam generation, absence of added sulphur in case of steam/aqueous pretreatment would be important. Although the acid use is about the same in both processes, acid is easily recoverable from the hydrolyzed, concentrated, and clarified extracts. With particle size reduction prior to extraction, the aqueous process gives almost 90% recovery of xylose, superior to dilute acid[2] or steam explosion-based extraction. In addition, the aqueous extraction at moderate temperatures around 170°C, as employed here, offers the possibility of isolation of xylan oligomers for alternate uses.[11,16]

References

1. Atchison, J. E. 1992. The rapid cooking horizontal tube continuous digester with screw feeder. Sugar y Azucar **87**: 94–102.
2. Bernhardt, H. W., Proudfoot, S. 1990. Dilute acid hydrolysis of bagasse and fermentation of the hydrolysate to produce single cell protein. Proc. S. Afr. Sugar Technol. Assoc. **64**: 150–153.
3. du Toit, P. J., Olivier, S. P., van Bijon, P. L. 1984. Sugar cane bagasse as a possible source of fermentable carbohydrates. I. Characterization of bagasse with regard to monosaccharide, hemicellulose and amino acid composition. Biotechnol. Bioeng. **26**: 1071–1078.
4. Hartfield, S., Hester, R. 1993. Separation of acid and sugar by ion exclusion chromatography. An application in the conversion of cellulose to ethanol, pp. 1078–1090. Proceedings of the First Biomass Conference of the Americas. National Renewable Energy Laboratory, Golden, CO.
5. Kaar, W. E., Cool, L. G., Merriman, M. M., Brink, D. L. 1991. The complete analysis of wood polysaccharides using HPLC. J. Wood Chem. Techol. **11**: 447–463.
6. Kaar, W. E., Brink, D. L. 1991. Simplified analysis of acid soluble lignin. J. Wood Chem. Techol. **11**: 465–477.
7. Nagaty, A., El-Sayed, O. H., Ibrahim, S. T., Mansour, O. Y. 1982. Chemical and spectral studies of hemicelluloses isolated from bagasse. Holzforschung **36**: 29–35.
8. Overend, R. P., Chornet, E. 1987. Fractionation of lignocellulosics by steam-aqueous pretreatments. Phil. Trans. Royal Soc. Lond. **A321**: 523–536.
9. Paturau, J. M. 1989. By-products of the cane industry. Elsevier, Amsterdam.
10. Purchase, B. S., Walford, S. N., Waugh, E. J. 1986. An update on progress in the production of ethanol from bagasse. Proc. S. Afr. Sugar Tech. Assoc. **60**: 33–36.
11. Rauschenberg, N., Dhara, K., Palmer, J., Glasser, W. G. 1990. Xylan derivatives from steam-exploded lignocellulosic resources—structure and properties. Polym. Preprints **31**: 650–652.
12. Reid, M. J., Rein, P. W. 1983. Steam balance for the new Felixton II mill. Proc. S. Afr. Sugar Technol. Assoc. **57**: 85–91.
13. Sanchez, P. 1990. Procede de production de sirop de xylose par hydrolyse acide de sorgho, Ph.D. dissertation, L'Institute National Polytechnique de Toulouse, Toulouse, France.
14. Saska, M., Clarke, S. J., Wu, M. D., Iqbal, K. 1992. Glucose–fructose equilibria on Dowex Monosphere 99 CA resin under overloaded conditions. J. Chromatogr. **590**: 147–151.
15. Saska, M., Wu, M. D., Clarke, S. J., Iqbal, K. 1992. Continuous separation of sugarcane molasses with a simulated moving bed adsorber. Adsorption equilibria, kinetics and application. Sep. Sci. Technol. **27**: 1711–1732.
16. Stscherbina, D., Philipp, B. 1991. Neuere ergebnisse zur isolierung, modifizierung und anwendung von xylanen. Acta Polymerica **42**: 345–351.
17. Torget, R., Werdene, P., Himmel, M., Grohman, K. 1990. Dilute acid pretreatment of short rotation woody and herbaceous crops. Appl. Biochem. Biotechnol. **24/25**: 115–126.
18. Wankat, P. 1986. Large scale adsorption and chromatography. CRC Press, Boca Raton, FL.