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THE SACCHARIFICATION of AGRICULTURAL RESIDUES[1]

A Continuous Process

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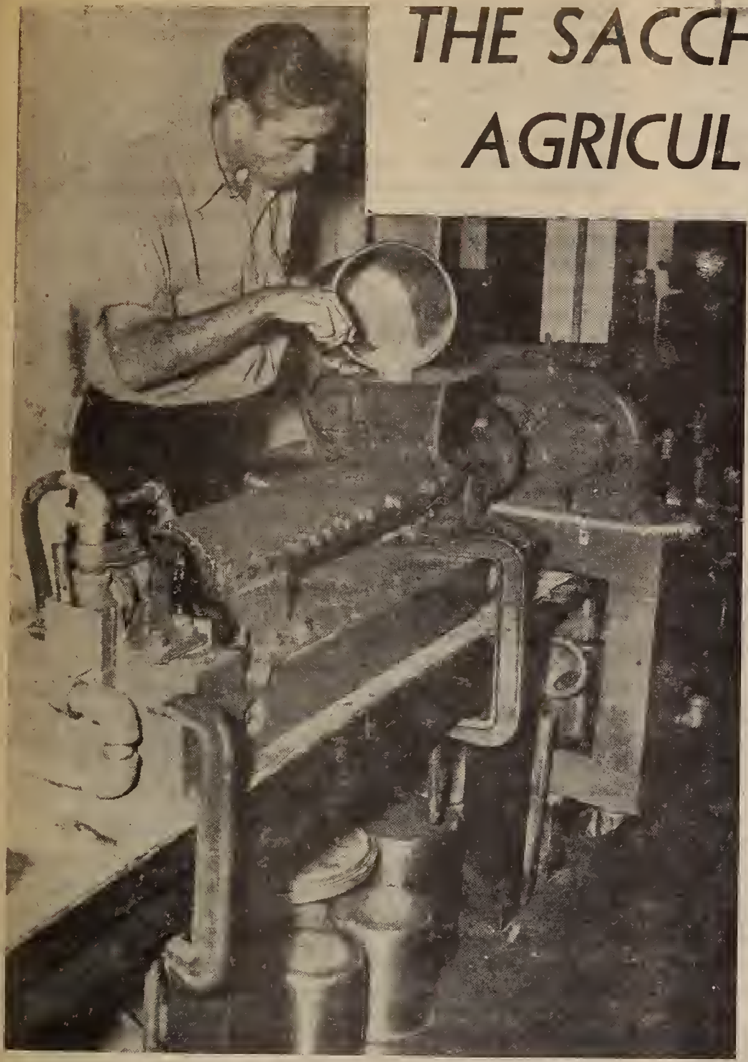

¶ Because of the chemical composition and physical properties of agricultural residues, they may find a unique place in the field of industrial saccharification. A continuous process for the saccharification of agricultural residues which makes use of these properties has been developed through a large-scale laboratory stage. This process is a two-stage operation in which the pentosans are first hydrolyzed by dilute acid. The cellulose is then saccharified by a new concentrated acid method which uses less than one fourth the amount of acid required by other known concentrated acid processes. The lignin remains as an insoluble residue. The methods employed enable almost quantitative separation of pentosans and cellulose. The pentosan hydrolysis yields a 15 to 20% xylose solution. The cellulose hydrolysis yields a 10 to 12% dextrose solution. The dextrose, which is obtained in yields of 85 to 90% of theoretical, is readily fermented by *A. aerogenes* and yeast. The machine used in this work for impregnating residues with acid is shown in the photograph at left.

THE logical raw material for the lowest-cost manufacture of fermentable sugars has always appeared to be wood because of its relatively high cellulose content and its apparent abundance in the form of waste from the lumber and pulp industries. Wood sugars in this country, however, have not been competitive in cost with blackstrap molasses as a fermentable sugar source. This may indicate the need of some new "added ingredient" in the economics of manufacture and in the merchandizing of all of the hydrolytic products.

Agricultural residues, or farm wastes, represent an annual cellulose reserve. It is estimated that 100 million tons of such residues might be available in this country for industrial purposes each year, with an equal amount left on the farms for plowing back into the soil. In view of the decrease in irreplaceable natural resources, it is becoming clear that at some period all countries must look to products of annual plant growth for the production of many materials now derived from other sources.

Of the many patented and developed industrial uses for agricultural residues, those only have survived the impact of technology and economics which have produced a superior product in their own right. The point of view of this Laboratory, to which the problem of industrial utilization of agricultural residues has been assigned, has been to depart from past efforts to use residues mainly as substitutes and rather to determine in what manner their inherent properties will perform an industrial duty better than other raw materials.

The bulky character of most residues, their high pentosan content, and particularly their lower cellulose content as compared with wood, have prevented their consideration as a source of raw material for saccharification. On the other hand, the higher density and greater cellulose content of wood have not guaranteed the economic success of saccharification processes. Perhaps the needed "added ingredient" is the concurrent production of a product which commands a higher price than the fermentable sugar. This might be furfural, now manufactured to the extent of about 20,000 tons per year, or xylose, which has potential uses if priced near sucrose. Both of these chemicals are derived from pentosans which generally occur in higher amounts in agricultural residues than in wood. An important limiting factor in wood saccharification processes is the slowness of diffusion of sugar solutions from chips. The porous character of residues largely eliminates this factor. By capitalizing on these properties of agricultural residues, which in the past have been considered as outstanding deficiencies, it might be possible to develop a saccharification process to produce fermentable sugars which could compete with blackstrap molasses.

Analyses made by this Laboratory of representative samples of different agricultural residues, together with analyses of typical

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hardwoods and softwoods, are given in Table I. It is apparent that a successful saccharification process in which agricultural residues are used must, in addition to dextrose or alcohol, produce xylose or furfural which sell at a higher price than dextrose. It would also be desirable to produce lignin in a usable form. Agricultural residues are more suitable than wood for such a process because the composition and density of wood prevent a clean-cut hydrolytic separation of C_5 and C_6 sugars.

The work has been carried through the first three of the six recognized process development steps: (1) Fundamental studies which sought (*a*) a method of quantitatively separating the pentosans from the lignocellulose and (*b*) a method of obtaining as nearly quantitative yields of dextrose as possible from the pentosan free lignocellulose. (2) Process studies based on the fundamental data so acquired; the process was envisioned as being continuous, involving low equipment and steam costs, requiring relatively short time cycles, and producing xylose and dextrose in relatively concentrated solutions. (3) Preliminary cost studies to determine whether semi-works or industrial scale operations would be justified.

FUNDAMENTAL STUDIES

Five agricultural residues—corncobs, sugar-cane bagasse, flax shives, oat hulls, and cottonseed hulls—were used in this development. Since optimum reaction conditions as well as yield of products from all five residues were similar, only the data on corncobs will be reported.

The Shaffer-Hartmann method (*14*) was used for the quantitative determinations of reducing sugars. The distillation method of the Association of Official Agricultural Chemists (*1*) was used for the conversions of pentosan to furfural, which was then determined by the low-temperature bromide method (*8*).

Pentosan Hydrolysis. Studies on pentosan hydrolysis were conducted to determine the conditions for maximum yield of pentoses with minimum yield of hexoses. Variables studied were acid concentration, temperature, time, solid to liquid ratio, and degree of fineness of the residues. These experiments were conducted at atmospheric pressure in 5-liter flasks equipped with reflux condensers, and at elevated pressures in 2-liter Erlenmeyer flasks in a steam-heated autoclave.

The data show that under several sets of conditions the pentosans may be hydrolyzed into soluble products almost quantitatively, while the cellulose is solubilized only slightly. For example, 95% of the pentosans of corncobs can be converted to xylose, together with a small amount of furfural, by digestion for 50 minutes in 4.4% sulfuric acid at 100° C. at a 6:100 solids to liquid ratio; the same yield is obtained at 121° C. by digestion for 50 minutes in only 0.98% sulfuric acid, with the same solids to liquid ratio. When the solids to liquid ratio at 121° C. is increased from 6:100 to 30:100, the sulfuric acid concentration must be increased from 0.98 to 1.9% to obtain 95% hydrolysis. Varying the degree of fineness of cobs between 2 and 10 mesh had little effect upon the rate of hydrolysis or the yield of products.

Hydrolysis data are summarized in Figure 1 and Table II. Data obtained at 121° C., with 1.9% sulfuric acid but with a solids to liquid ratio of 6:100, are included in Figure 1. Under these conditions the calculated conversion of pentosans to soluble hydrolytic products totals 109%, the excess percentage being attributed to partial hydrolysis of the cellulose.

The data in Table II, which are representative of those obtained in a number of experiments, illustrate the degree of fractionation of pentosans from hexosans possible at 100° and 121° C. Thus, within certain limits conditions which gave 95% theoretical conversions of the pentosans to hydrolytic products also gave almost quantitative separations of the pentosans from the hexosans. It is indicated that, in order to obtain the sharpest fractionation of the pentosans from hexosans, hydrolytic conditions must be rigidly controlled.

Cellulose Hydrolysis. The analyses of the corncobs before and after hydrolysis are shown in Table III; 43.9% of the dry matter, consisting of xylose, furfural, acetic acid, soluble gums, ash, and some unidentified materials, was removed from the cobs by hydrolysis. The data show that the extracted cobs were relatively rich in cellulose and lignin but poor in pentosans. This residue was porous and friable when dry.

In determining the cellulose content of the extracted cob residues, some observations were made which had considerable bearing on the choice of a method for hydrolyzing the cellulose. In applying the standard 72% sulfuric acid method (*12*) to the determination of lignin and cellulose, it seemed advisable to study the rate of saccharification. The residues were digested in different amounts of 72% sulfuric acid at 10° C. for various times. Sufficient water and, if necessary, sulfuric acid were added to each sample to make 1200 ml. of a 4% acid solution. The solutions were then hydrolyzed at 121° C. for 45 minutes.

The rate of saccharification of the cellulose in the extracted cobs was considerably greater than that of the original cobs. This was attributed to the much greater porosity of the extracted material. Quantitative yields of dextrose could be obtained from the extracted corncobs by considerably less 72% sulfuric acid than was required by the unextracted cobs. Commendable yields of dextrose were obtained by mixing less than one part of 72% sulfuric acid, small portions at a time, into one part of extracted cobs, followed by the hydrolysis procedure.

In view of these results a process based on treatment of the extracted cobs, first with small amounts of concentrated sulfuric acid and then by dilution with water and hydrolysis at atmospheric or increased pressure, warranted further investigation. It was hoped by this method that reversion of glucose to nonfermentable compounds would be reduced to a minimum and that more nearly quantitative yields of dextrose could be obtained.

In preliminary experiments varying amounts of 80% sulfuric acid were mixed into 100 parts of the extracted corncobs. These samples were triturated at room temperature with a mortar and pestle for a few minutes. In later experiments larger samples were triturated on a rubber mill. Ten grams of the triturated samples were mixed with a liter of 8% sulfuric acid and hydrolyzed at 121° C. for 45 minutes. Data summarizing the yields of dextrose are given in Figure 2.

These data show that the cellulose can be converted to dextrose in about 90% yield of theory by triturating 100 parts of washed, dry extracted cob residue with 125 parts of 80% sulfuric acid at room temperature, followed by hydrolysis in 8% sulfuric acid solution at 121° C. for 45 minutes.

PROCESS DEVELOPMENT STUDIES

With conditions established which would give almost quantitative separation of pentosans from hexosans and by which their respective hydrolytic products could be obtained in at least 90% of theoretical yields, the problem of transforming these laboratory procedures into small-scale unit operations was undertaken. Large-scale laboratory apparatus and small pilot-plant equipment were used when available, but some equipment had to be designed and built. The operations in the final process were to be continuous and were to furnish relatively concentrated solutions of sugars. A flow sheet of the process is shown in Figure 3.

Corncob Grinding. Whole corncobs were ground in a commercial cob crusher to particles that passed a 4-mesh sieve.

Pentosan Hydrolysis. Since exploratory tests had indicated that the pentosan fraction of corncobs could be hydrolyzed by a countercurrent flow of hot, dilute sulfuric acid, it was thought that countercurrent extraction equipment might be suitable for this operation. Preliminary experiments were conducted, therefore, in a five-cell, laboratory-scale, glass diffusion battery which

Table I. Percentage Analysis of Representative Hardwoods, Softwoods, and Agricultural Residues

Material	Pentosan	Cellulose	Lignin
Pondsrosa pine (*11*)	7.4	52.3	26.6
·Tanbark oak (*11*)	19.6	44.8	24.8
Corncobs	28.1	36.5	10.4
Bagasse	20.4	41.3	14.9
Oat hulls	29.5	33.7	13.5
Cottonseed hulls	21.0	35.1	16.8
Flax shives	23.0	38.0	24.0

Table II. Effects of Acid Concentration, Temperature, and Time upon Separation of Pentosans from Hexosans

Acid concentration, %	1.9	4.4	4.4
Temperature, ° C.	121	100	100
Time, minutes	50	55	50
Solids:liquid ratio, grams/100 ml.	30:100	6:100	6:100
1. Yield of xylose, %	86.1	84.1	86.9
2. Yield of furfural (as xylose), %	9.3	10.9	8.4
3. Sum of 1 and 2	95.4	95.0	95.3
4. Yield of dextrose, %	0.78	3.2	1.4

had a corncob capacity of 4 pounds. Each cell was equipped with the necessary inlets and outlets and with an electric heating device. For each run the cells were charged with crushed corncobs; dilute sulfuric acid, at just below the boiling point, was then circulated through the battery. Sulfuric acid concentrations ranging from 4.9 to 9.8% and hydrolysis and extraction periods of 50 to 185 minutes were investigated. Experiments were not run at temperatures above 100° C. because the diffusion equipment was not constructed for pressure operation.

Hydrolyzates containing 14 to 20% reducing sugar were consistently obtained. From 90 to 95% of the pentosans, converted to reaction products, could be extracted from corncobs in 80 to 120 minutes, depending upon the concentration and flow rate of the dilute sulfuric acid. Rigidly controlled conditions were necessary, however, to obtain sharp fractionation of the pentosans from the cellulose. Data from three runs which show the effects of acid concentration and time upon this separation are given in Table IV. Although high yields of xylose were obtained under various conditions, a sharp fractionation of the pentosans from the hexosans was obtained only under limited conditions. The corncob residues from these runs retained little reducing sugar. From fifteen runs the residue retained an average of 0.14% of the sugar produced during hydrolysis.

On the basis of this information and of more recent studies on design a semiwork-scale pentosan hydrolyzer is now under construction. This larger-scale hydrolyzer will allow a wider range and more rigid control of the process variables than was possible in the small laboratory diffusion battery, and will also make it possible to obtain cost data on this method of producing relatively concentrated solutions of xylose.

Drying of Extracted Corncob Residue. The solid residues from this extraction were readily filtered and could be reduced to 75% moisture on a Büchner funnel under vacuum. Studies have shown that the moisture content may be reduced to 47% by commercial dewatering machines.

Since the cellulose hydrolysis step to follow requires 80 to 85% sulfuric acid and low temperature, it is obviously impractical to add concentrated acid to the wet residue. It is desirable to make use of the acid left in the residue, and a study was made to determine drying conditions which would not destroy the lignocellulose. A small dryer in which hot air could be forced through a layer of solids was used. Air temperatures between 30° and 150° C. were investigated. The experiments on drying were controlled so that the original dilute sulfuric acid was concentrated to 72% as determined by loss in weight. Lignocellulose residues which had been dewatered to 50% could be rapidly dried in this equipment at solids temperatures up to 80° C. with no decomposition. It was further discovered that these residues, dried in the presence of acid, are saccharified more readily than residues dried in the absence of acid.

Impregnation with Concentrated Sulfuric Acid. Although several types of equipment might have been used for impregnating these residues with concentrated acid, previous work by one of the authors on a similar problem (*3*) led to the selection of the principle of the oil expeller, which permits continuous operation under maintained and controlled high pressure on the solids being processed.

The impregnating machine (shown in the photograph on page 24) was constructed of mild steel and had a capacity of 40 pounds of dried residue per hour. It consisted of a feed hopper, a discontinuous screw on a water-cooled shaft, and a water-jacketed casing. By changing the temperature of the cooling water, it was possible to operate the impregnator at temperatures ranging from 10° to 100° C. The discontinuous screw was constructed by intercepting the screw flight after each complete turn, a distance of about 1.5 inches being left between each flight. The volume of each succeeding flight was decreased slightly so that the volume of the last worm had a capacity about one third that of the first or feed worm. The pitch of each worm flight was calculated from lignocellulose compression data. The data obtained from extracted corncobs showed that a pressure of 175 pounds per square inch compressed this residue to about 35% of its initial volume. Greater pressures compressed the residue only slightly more. These conditions were used, therefore, in designing the discontinuous screw. The impregnator was driven by a variable-speed drive which permitted a study of retention times ranging from 2 to 8 minutes.

To study acid impregnation of the residue in this machine, about one ton of corncobs had to be hydrolyzed with dilute acid. Since the laboratory diffusion hydrolyzer was far too small for this job, batch pentosan hydrolyses were conducted in a 150-gallon, glass-lined kettle equipped with an agitator.

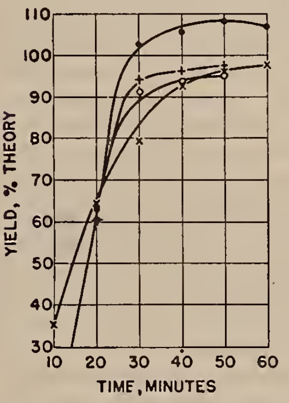


Figure 1. Effect of Variables on Yield of Conversion Products (Calculated as Xylose) from Pentosan Hydrolysis

	Acid Concn., %	Temp., ° C.	Solids/Liquid Ratio, Wt./Vol.
×	4.4	100	6:100
○	1.9	121	30:100
●	1.9	121	6:100
+	0.98	121	6:100

Table III. Percentage Analysis of Corncobs before and after Hydrolysis

Material	Whole Corncobs	Extd. Corncobs
Pentosans	28.1	2.49
Cellulose	36.5	65.1
Lignin	10.4	18.5
Ash	1.48	...
Alcohol-benzene solubles	6.20	...
Unidentified	17.32	13.91

Table IV. Hydrolysis and Extraction of Pentosans from Corncobs in a Diffusion Battery

Acid concentration, %	8.8	7.3	5.8
Temperature, ° C.	98.0	98.0	98.0
Time of extn. per cell, min.	105.0	125.0	129.0
1. Xylose in hydrolyzate, % of theory	83.8	80.0	86.8
2. Furfural as xylose in hydrolyzate, % of theory	8.8	9.1	7.9
3. Sum of 1 and 2	92.6	89.1	94.7
4. Dextrose in hydrolyzate, % of theory	11.6	4.2	0.0
5. Xylose in residue, % of theory	3.4	5.6	5.6
6. Dextrose in residue, % of theory	85.1	88.0	94.5
7. Total xylose, 3 plus 5	96.0	94.7	100.3
8. Total dextrose, 4 plus 6	96.8	92.2	94.5
9. Concn. of reducing sugar in hydrolyzate	22.9	18.5	14.2

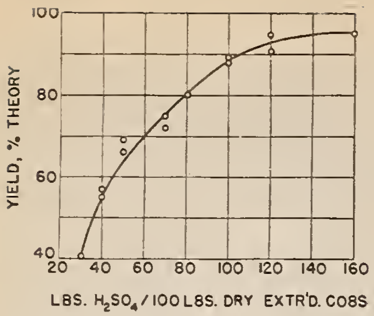


Figure 2. Effect of Acid-Residue Ratios on Yield of Dextrose from Extracted Corncobs

Optimum conditions for small-scale batch hydrolysis were used. The hydrolyzed charges were dropped into a wooden box and then transferred to 20-gallon stoneware vacuum filters. The dilute acid content of the solids was reduced to 50–55% by dewatering in a large hydraulic press. The filtrate was used for studies on xylose and furfural.

The pressed residue was dried in 400-pound batches at 60° to 70° C. in a large hot-air dryer and then ground in a hammer mill to pass screens of different mesh. To illustrate the ease of grinding this material, one pass through a hammer mill equipped with a screen having $^1/_8$-inch round holes produced a material 82% of which passed a 40-mesh sieve.

The impregnation runs consisted of mixing about 2-pound portions of the dried and ground residue with different amounts of sulfuric acid of various concentrations in a 3-gallon batch mixer equipped with a duplex turbine agitator and a water jacket. This acid-residue mixture was fed by hand to the impregnator. The acid-impregnated material was then hydrolyzed in 8% sulfuric acid at 121° C. for 45 minutes, and the percentage of conversion of cellulose to glucose was determined analytically. A 5-gallon Hastelloy autoclave was used for hydrolysis because of the desirability of handling relatively large batches of material. This assembly of equipment allowed a thorough investigation of the many process variables, including fineness of lignocellulose residue, amount of acid dried into it, amount, concentration, and temperature of sulfuric acid mixed with the residue, and temperature and time of the impregnation operation.

Data obtained are shown in Figure 4. Residues from which the acid was washed did not give such high yields of dextrose as residues in which the acid was dried. Other optimum conditions (curve 1, Figure 4) were 85% concentration of sulfuric acid, a fineness of 40 to 60 mesh, and an impregnation time of 2 minutes at 40° C. A 90% yield of dextrose is obtained by treating 100 parts of the dried residue with a total of 48 parts of sulfuric acid, equivalent to 27 parts of sulfuric acid per 100 parts of initial corncobs. This amount of acid is considerably less than that suggested by other concentrated sulfuric acid saccharification processes (*2*, *10*, *16*, *17*). Less than 5 minutes is required for the action of this amount and concentration of acid, as compared with the 4–10 hours required by other methods. The primary reasons for the effectiveness of this small amount of acid lies in the great absorptive capacity of the dried, acid-containing residue and in the method of dispersing the concentrated acid throughout its cellular structure.

One might expect that mixing 53 parts of 85% sulfuric acid with 100 parts of dry solids would result in a pasty mass. That the resulting mixture is a dry, easily flowing powder is illustrated in Figure 5. This mixture is being poured from the bottle on the right, while the acid dried residue is being poured from the other bottle. When this free-flowing mixture is subjected to the constantly changing directional pressure of the impregnator for 2 minutes at 40° C., the result is the homogeneous plastic mass at the bottom. It is evident that the physical relation between the solid particles and the acid has changed during the impregnation step. The yield of reducing sugar obtainable from the impregnated mixture is 30% higher than that from the nonimpregnated mixture.

Dilute Acid Hydrolysis. After the optimum conditions for the operation of the impregnator had been established, a study was undertaken to determine the conditions for the hydrolysis of the acid-degraded lignocellulose material that would result in obtaining relatively concentrated dextrose solutions in the highest yields. Different amounts of water were added to 1000-gram samples of the acid-impregnated residues to give concentrations of sulfuric acid ranging from 1 to 18%. These slurries were hydrolyzed at temperatures from 100° to 155° C. The optimum conditions were a 7–10 minute hydrolysis in 8% sulfuric acid at temperatures between 120° and 130° C. Under these conditions hydrolyzates containing 10.5% dextrose were obtained. Data in Figure 6 summarize the effects of these variables on yields of dextrose.

Loss of Sugars in Filter Cakes. If the pentosan hydrolyzate is used for industrial fermentation, the residual acid must be neutralized with lime. In turn, the lignin must be filtered from the hexosan hydrolyzate and the acid in this filtrate must be neutralized with lime. Preliminary filtration studies made in cooperation with filter manufacturers have indicated the order of the loss of sugars in the cakes.

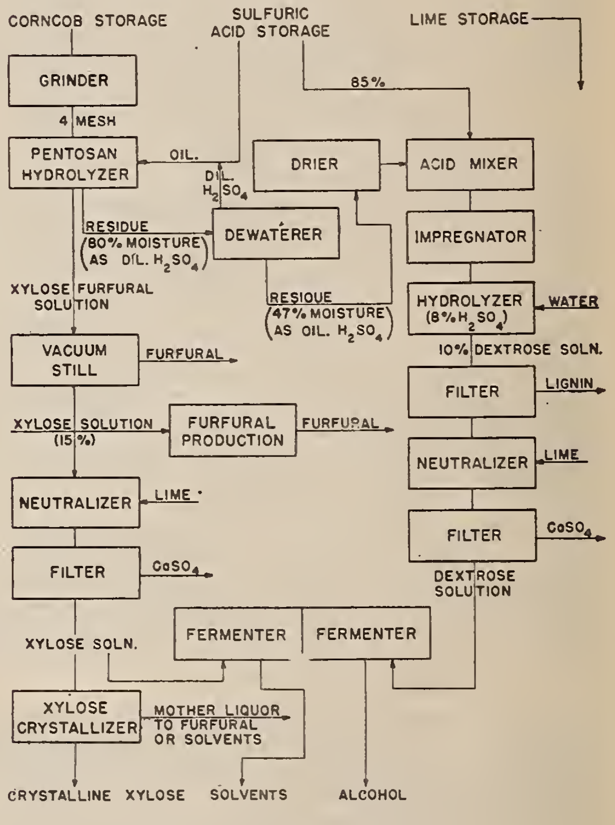


Figure 3. Flow Sheet of the Process

By using a leaf filter with the pentosan hydrolyzate, it was found that an amount of wash water equal to about 90% of that required for pentosan make-up gave a calcium sulfate cake free of sugar. In the semiworks plant this wash water will serve as the major part of the make-up for the 4.4% sulfuric acid used in the pentosan hydrolysis.

In the case of the hexosan hydrolyzate, by using wash water equivalent to 30% of the amount required for make-up in the final hydrolysis step, 2.2% of the total sugar remained in the lignin cake. When 36% of the amount of make-up water required in

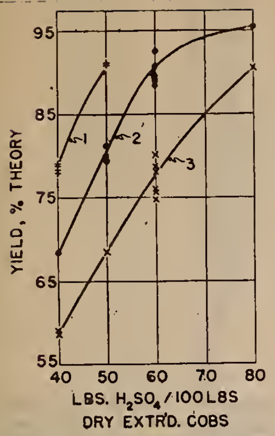


Figure 4. Effect of Variables on Yield of Dextrose from Extracted Corncobs Impregnated with 85% Sulfuric Acid at 40° C.

- × 8-mesh residue, water-washed, and dried
- ● 50-mesh residue, water-washed, and dried
- + 50-mesh with acid dried into residue

the final hydrolysis step was used as a wash for the calcium sulfate cake, 0.27% of the total sugars in the original hydrolyzate was held in the cake. Analyses of the final hydrolyzate before filtration have indicated that 88% of the cellulose is consistently obtained in the form of dextrose. Assuming the filter cake loss reported, the dextrose solution ready for fermentation is equivalent to a yield of 85.5% of theory. These losses could be decreased in cyclic semiwork operations, since further washing of the lignin cake is possible without exceeding the make-up water required in the hydrolysis step.

Fermentation of Dextrose Solution. The dextrose solutions from this process, after removal of the lignin by filtration and neutralization of the sulfuric acid with lime, are readily fermented by yeast to alcohol. Amounts equivalent to 40–45 gallons of 95% alcohol have been produced per ton of dry corncobs. There are no indications of compounds toxic to yeast in these solutions. Preliminary studies on yeast fermentation indicated that some accessory factors were required for the initial growth of yeast on the hydrolyzates. These growth factors were supplied by incorporating 0.1% of corn steep liquor in the medium. Under these conditions fermentation efficiencies of 85–89% were obtained. Later studies indicate that other variations of standard fermentation practices may eliminate the necessity of adding the corn steep liquor to the medium.

Uses of Xylose Solution. The solution of xylose obtained from the countercurrent pentosan hydrolysis had approximately the following composition: xylose, 15%; dextrose, 0.3%; furfural, 1.75%; acetic acid, 2.0%; and sulfuric acid, 4.4%. The furfural may be removed by feeding the hot solution to a vacuum column and removing the furfural water azeotrope. There are several industrial outlets for xylose, each of which will be briefly discussed, together with the experimental studies conducted.

FERMENTATION. Fermentation of the xylose solution, freed of furfural and neutralized with lime, has not been extensively investigated. Sufficient information exists to indicate that, when it is mixed with about three parts of dextrose, commercial fermentation to butanol and acetone by *Clostridium acetobutylicum* will be satisfactory. Fulmer (*15*) reported normal yields of these solvents from pure xylose by this organism after incorporation of special nutrients in the medium. The solution may also be fermented to 2,3-butylene glycol by *Aerobacter aerogenes*. However, all these products are made as satisfactorily from glucose or from blackstrap molasses, so that the xylose in these fermentations is deemed to have no greater value than dextrose.

FURFURAL MANUFACTURE. Because of the present large market for furfural, which has never been priced at less than 9 cents per pound, first consideration has been given to it as a potential coproduct with dextrose or alcohol. Furfural may be manufactured from xylose solutions at elevated temperatures in commercial yields (*5*, *6*). Preliminary studies conducted in a 5-gallon Hastelloy autoclave equipped with a regulated steam sparger, steam jacket, and condenser show that it is possible to obtain at least 69% of the theoretical yield of furfural. This problem is under active study, looking to the design of a semi-works unit.

Table V. Products Obtainable from One Ton (Dry Weight) of Agricultural Residues

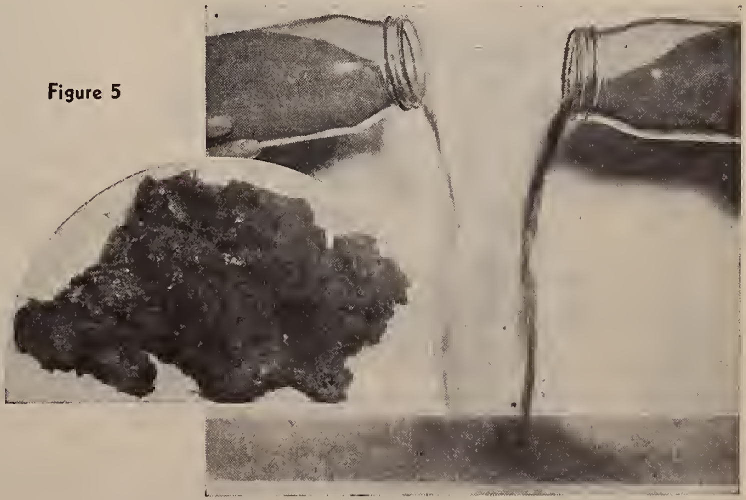
Agricultural Residue	93% Pure Crystalline Xylose, Lb.	Furfural, Lb.	95% Alcohol, Gal.	Lignin, Lb.
Corncobs	135	214	44	227
Bagasse	98	155	49	327
Oat hulls	141	224	42	295
Cottonseed hulls	101	160	42	332
Flax shives	111	175	46	525

CRYSTALLINE XYLOSE. At present there is no commercial production of xylose, but numerous inquiries have come to the Laboratory concerning its availability on a tonnage scale. Since xylose is the source of furfural and since yields of furfural from xylose-yielding materials on a commercial scale have never reached much above 60% of theoretical, it is evident that xylose could sell at about half the price of furfural and bring an equal financial return.

A number of investigations (*4*, *13*) have been undertaken with the object of producing xylose commercially, but the cost of manufacture has always been too high. These processes were directed toward obtaining xylose as a main product. LaForge and Hudson prepared crystalline xylose (*9*) by extracting corncobs first with hot water to remove interfering gums and then with dilute acid. When cobs were directly treated with acid, the gums interfered with crystallization. Preliminary studies in this Laboratory on xylose crystallization from the pentosan hydrolyzate confirmed this observation. In the semiworks, the ground cobs could be extracted with hot water continuously and result in lowering the total yield of sugars only about 1.5%. It has been possible to crystallize 25% of the xylose as a white product of 93% purity, from pentosan hydrolyzates prepared from hot-water extracted cobs. The mother liquors from this crystallization were used for studies on the production of furfural.

Gums which interfere with crystallization, together with acetic acid, can be removed from xylose solutions obtained from unwashed cobs by countercurrent extraction with butyl or isoamyl alcohol. When the xylose solution is used directly for the

Figure 5



Left, Acid-Dried Ground Residue; *Right,* Same Material after Mixing with 85% Sulfuric Acid; *Below,* after Passage through Impregnator manufacture of furfural, the acetic acid is recovered in the distillate. Semiworks equipment for studying methods of crystallizing xylose and recovering acetic acid will be obtained. In the meantime, questions relating to the use of xylose as a sweetening agent in food are being explored.

Lignin. The lignin residue may be filtered readily and dried to a friable powder. Some preliminary work with the lignin from this process indicates its possibilities as a component of plastics. It is known (7) that lignin may be hydrogenated to yield methanol and derivatives of propylcyclohexane. An extensive research program on valuation and use of the various by-products discussed is underway at this Laboratory.

COST ESTIMATES

Availability and Cost of Residues. The five residues studied collect as by-products at processing plants. In each case approximately 100,000 tons per year could be secured within a radius of 100 miles from suitable collection points. A survey of the availability and probable cost of corncobs in Illinois in 1941 indicated that they could be obtained from elevators at an average delivered price of $3.50 per ton. The average delivered price of flax shives in Minnesota was estimated to be between $3.50 and $4.00 per ton. Florida, where a 6-month sugar mill operation is carried on, should furnish bagasse at a lower cost than Louisiana which has a shorter grinding season. The cost of bagasse in Florida is estimated to be $5.00 to $6.00 per ton. Cottonseed hulls average close to $6.50 per ton. These are all prewar prices.

Preliminary Cost Estimates. It is obviously necessary to make some economic evaluation of the process to determine whether its study should be carried farther than the large-scale laboratory stage in which about one ton of corncobs was processed. The estimates given are based on experimental results and on data from unit operations.

Assuming that the process yields 25% of crystallized xylose of 93% purity, that the remainder of the xylose is converted to furfural in 69% yield, and that the dextrose is fermented by yeast to alcohol, the quantities in Table V are obtainable from the different residues studied during this saccharification development.

Thus, alcohol would be only one of several products that would result from the saccharification of agricultural residues. Assuming a selling price of 5 cents a pound for xylose, 9 cents a pound for furfural, 22 cents a gallon for alcohol, and $3.50 a ton for lignin as fuel, the products from one ton of corncobs would sell for $36.09. If 50% of the xylose could be crystallized and the remainder converted to furfural, the sales value of the products would be $36.36 per ton of cobs; if all the xylose were converted to furfural and all the dextrose fermented to alcohol, the sales value would be $34.65 per ton of cobs.

The approximate costs of operation may be estimated from the following conversion costs: 0.5 cent per pound to crystallize and dry the xylose; 1.0 cent per pound to convert the xylose to furfural; and 5 cents per gallon for producing 95% alcohol. The chemical costs of saccharification will be $5.00 per ton of corncobs. The labor, fixed charges, and other operating costs are estimated at $5.00 per ton. For the purpose of present estimates the cost of corncobs is set at $6.00 per ton. On the basis of these cost figures the conversion costs and sales values of the products per ton of cobs are shown in Table VI. The difference between sales value and costs represents the money available for sales and other administrative expenses and for profit. It is evident that it would be desirable to develop markets for crystalline xylose or derivatives as well as larger markets for furfural.

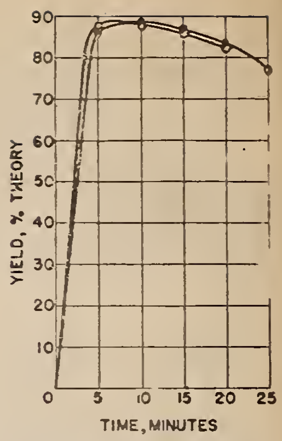


Figure 6. Effect of Time and Temperature on Dextrose Yields from Impregnated Residues by Hydrolysis in 8% Sulfuric Acid

● 121° C., ○ 130° C.

Table VI. Estimates of Conversion Costs and Sales Value of Products per Ton of Corncobs

	25% Xylose as Crystals		50% Xylose as Crystals		No Xylose	
	Amount	Sales value	Amount	Sales value	Amount	Sales value
Xylose, lb.	135	$ 6.75	270	$13.50	...	...
Furfural, lb.	214	19.26	142	12.78	273	$24.57
Alcohol, gal.	44	9.68	44	9.68	44	9.68
Lignin, lb.	227	0.40	227	0.40	227	0.40
Total value		$36.09		$36.36		$34.65
	Amount	Conversion costs	Amount	Conversion costs	Amount	Conversion costs
Xylose, lb.	135	$0.67	270	$1.35	...	....
Furfural, lb.	214	2.14	142	1.42	273	$2.73
Alcohol, gal.	44	2.20	44	2.20	44	2.20
Chemicals	...	5.00	...	5.00	...	5.00
Corncobs	...	6.00	...	6.00	...	6.00
Fixed charges	...	5.00	...	5.00	...	5.00
Total costs	...	21.01	...	20.97	...	20.93
Sales value	...	36.09	...	36.36	...	34.65
Difference for sales expense, administration, & profit	...	15.08	...	15.39	...	13.72

Since the sales prices given are prewar values and the conversion and other costs are believed to be conservative, the process is considered sufficiently interesting for semiworks study. The semiworks to be constructed will be capable of processing 3.3 tons of corncobs in an 8-hour day, producing one ton of glucose, about 1600 pounds of xylose, 200 pounds of furfural, and 1000 pounds of lignin. The production of crystalline xylose and the conversion of xylose to furfural will be studied. The dextrose solutions will be fermented by yeast to alcohol, and the xylose solutions, or combination of the dextrose and xylose solutions, will be fermented to butanol and acetone, 2,3-butylene glycol, or other products by appropriate organisms. The alcohol pilot plant at the Laboratory has a capacity of 500 gallons of alcohol per day and is fully equipped for all these fermentation operations. The joint operation of the semiworks and the pilot plant should establish accurate operating and cost data.

LITERATURE CITED

(1) Assoc. of Official Agr. Chem., Methods of Analysis, 5th ed., p. 361 (1940).
(2) Dreyfus, H., U. S. Patent 1,919,623 (July 25, 1933).
(3) Dunning, J. W., and Fulmer, E. I., unpub. data, Iowa State College, 1938.
(4) Firstenberger, B. F., *Iowa State Coll. J. Sci.*, 18, 27 (1943).
(5) Foster, L. F., *Ibid.*, 8, 191 (1933).
(6) Fulmer, E. I., Christensen, L. M., Hixon, R. M., and Foster, R. L., *J. Phys. Chem.*, 40, 1933 (1936).
(7) Harris, E. E., D'Ianni, J., and Adkins, H., *J. Am. Chem. Soc.*, 60, 1467 (1938).
(8) Hughes, E. E., and Acree, S. F., Ind. Eng. Chem., Anal. Ed., 6, 318 (1934).
(9) LaForge and Hudson, Ind. Eng. Chem., 10, 925 (1918).
(10) Oxley, H. F., Groombridge, W. H., and Challis, W. (to Celanese Corp.), U. S. Patent 1,964,646 (June 26, 1934).
(11) Ritter, G. J., and Fleck, L. E., Ind. Eng. Chem., 14, 1050 (1922).
(12) Ritter, G. J., Seborg, R. M., and Mitchell, R. L., Ind. Eng. Chem., Anal. Ed., 4, 202 (1932).
(13) Schreiber, W. T., Geib, N. V., Wingfield, B., and Acree, S. F., Ind. Eng. Chem., 22, 497 (1930).
(14) Shaffer, P. A., and Hartmann, A. F., *J. Biol. Chem.*, 45, 365–90 (1921).
(15) Underkofler, L. A., Christensen, L. M., and Fulmer, E. I., Ind. Eng. Chem., 28, 350 (1936).
(16) Waldhof, Z., Brit. Patent 147,415 (Oct. 7, 1921).
(17) Wohl. A., *Ibid.*, 146,860 (April 21, 1921).

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