⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 074 983**
B1

⑫ EUROPEAN PATENT SPECIFICATION

㊺ Date of publication of patent specification: **05.11.86**

(51) Int. Cl.^{4}: **C 13 K 1/02,** D 21 C 3/20

㉑ Application number: **82900956.2**

㉒ Date of filing: **26.03.82**

(86) International application number:
PCT/EP82/00068

(87) International publication number:
WO 82/03409 14.10.82 Gazette 82/25

(54) HIGH EFFICIENCY ORGANOSOLV SACCHARIFICATION PROCESS.

㉚ Priority: **26.03.81 US 248023**
09.02.82 CA 395820

㊸ Date of publication of application:
30.03.83 Bulletin 83/13

㊺ Publication of the grant of the patent:
05.11.86 Bulletin 86/45

(84) Designated Contracting States:
AT BE CH DE FR GB LI NL SE

㊿ References cited:
WO-A-82/00483
CH-A- 202 534
GB-A- 416 416
GB-A-2 003 478

Chemical Abstracts, vol. 91, no. 18, October 28, 1979 (Columbus, Ohio, US) Koell Peter et al.: "Thermal degradation of birch wood with supercritical gases (organic solvents) in a high-pressure, high-temperature flow apparatus: the liquefaction of wood and further evidence for an alternative cellulose pulp technology", see page 74, abstract no. 142251k, Holzforschung 1979, 33(4), 112-16

(73) Proprietor: **Bau- und Forschungsgesellschaft**
Thermoform A.G.
Ryfstrasse 50
Murten/ Fribourg (CH)

(72) Inventor: **PASZNER, Laszlo**
3906 West 33rd Avenue
Vancouver British Columbia (CA)
Inventor: **CHANG, Pei-Ching**
180 West 22nd Avenue
Vancouver British Columbia (CA)

(74) Representative: **Hansmann, Axel**
Patentanwälte HANSMANN & VOGESER Albert-Rosshaupter-Strasse 65
D-8000 München 70 (DE)

Courier Press, Leamington Spa, England.

Description

The invention relates to a process for the production of sugars from particulate cellulose material by treating the material in a pressure vessel with a mixture of acetone and water containing a small amount of an acidic compound at elevated temperatures.

Such a process wherein an acidified 30 to 70% by volume acetone containing mixture of acetone and water is used as the cooking liquor is described in GB—A—2003478.

Further GB—A—416416 describes the recovery of cellulose by the extraction of lignin from a lignocellulose material with acetone or a mixture of acetone and water.

The object of the invention is to rapidly and quantitatively solubilize and recover sugars from cellulosic materials.

This object is attained by the process of the claims.

Unexpectedly it has been found that acetone in volume concentrations in water of greater than 70% with a catalytic amount of an acid greatly accelerates the hydrolysis rates of cellulosic materials at elevated temperatures by sugar-acetone-complex formation. In addition there is substantially no degradation of sugars during the saccharification process at the selected conditions, although the acetone complexes are found to hydrolyse roughly 500 times faster than the alkyl glucosides and polyglucan described in the prior art. Further benefit of the acetone-sugar-complexes is their facile separation into individual sugar species based on such simple processes as volatilization, selective hydrolysis and liquid-liquid extraction. Complex formation of monomeric sugars in anhydrous acetone in the presence of mineral acids at room temperature is described in Methods in Carbohydrate Chemistry, Vol. II, pp. 318.

The term "cellulosic material" includes materials of vegetable and woody origin, i.e. cellulose and lignocellulose materials.

The acidic compounds can be of inorganic or organic origin and should be inert with respect to the solvent. Strong inorganic acids as sulfuric, hydrochloric and phosphoric acids are preferred; acidic salts such as aluminum chloride and sulfate, ferric chloride and organic acids such as trifluoroacetic acid can also be used. For very rapid hydrolysis acid concentrations of 0.04 to 0.06 normal, acetone concentrations of about 80% and temperatures over 200°C can be used. However, for near theoretical sugar yields, low acid concentration of 0.02 normal and less, high acetone concentration of above 80% and high temperature of above 200°C are most suitable.

Preferably reaction vessels with inert linings are used to eliminate the sugar degradation catalyzing effects of transition metal ions such as Ni, Co, Cr, Fe and Cu which may be components of metallic vessel walls, tubing and other control elements with which the hot liquor comes into contact.

Notwithstanding these process options the recovery of pentoses from the reaction mixture is generally by flash-evaporation of the major fraction of the acetone first with continued distillation under reduced pressure or by steam stripping to yield the pentose sugar complexes in the distillate. Separation of pentoses and hexoses by such simple means is made possible by the largely differing boiling points of their acetone-sugar complexes which form even in the presence of water during the high temperature hydrolysis step in the process of the invention provided the acetone concentration exceeds 70% by volume.

After hydrolyzing the cellulosic material at elevated temperature for a limited period of time, it is very important, that the temperature of the reaction mixture be rapidly lowered to under 100°C to avoid unwanted degradation of the sugars. This is best accomplished by controlled flashing-off of the volatiles since sugar degradation was found to be insignificant below the boiling point of water even in the presence of dilute acids. Usually, the cooling of the liquor can be continued to ambient temperatures or less (25°C) before fermentation or further processing.

The above described process can be operated in continuous or semi-continuous manner using batch cooking principles for the latter. Semi-continuous saccharification would employ a battery of pressure vessels each at various stage of hydrolysis to simulate a continuous process. In continuous operation, all stages of hydrolysis are accomplished in a single pressure vessel and the product mix is always determined by the particular saccharification program set. Comminuted wood solids and the cooking liquor are fed continuously to the pressure vessel at such a rate that the time elapsed between feeding and exit of the products would not exceed that determined earlier to obtain 50% hydrolysis of solid residue at any one stage considered for the process. Thus the residence time would be always fitted to the most sensitive stage in order to provide sugar recoveries exceeding 90% for that particular stage. The three major stages of saccharification to be considered are:

(a) bulk delignification and pre-hydrolysis; during this stage up to 75% of the lignin and 95% of the governing hemicelluloses (xylose in hard-woods and mannose in soft-woods) may be removed. The solid residue yield is invariably above 50% of the starting material;

(b) continued delignification and cellulose purification stage; during this stage delignification is largely completed and the rest of the hemicellulose sugars and some of the amorphous glucan are removed. The solid residue at this stage is generally less than 35% and is predominantly crystalline in nature;

(c) proceeding to total saccharification; the residual cellulose of stage (b) is decomposed to monomeric sugars. This step may take more than one liquor change to accomplish a better than 90% sugar recovery.

In continuous operation liquors collected from the various stages of hydrolysis may contain sugars from all stages (a) to (c) which is the situation with an apparatus having no means of separating the top pre-hydrolysis liquor from the rest of the liquor pumped in with the chips. With the present invention such separation for purification of the sugars is unnecessary because the sugars occur as complexes, pentoses having a different volatility than the hexose sugars with which they may be mixed. The lignin is separated on basis of its insolubility in water and is recovered outside the reactor on flash-evaporation of the organic volatiles.

In practical hydrolysis, based on the semi-continuous process, five liquor changes would be required to cause total saccharification and dissolution and provide mass recoveries better than 95%. The preferred liquor-to-wood ratio is 7:1 to 10:1. Due to the shrinking mass bed the total amount of liquor required for hydrolysis of 100 kg of aspen wood at a constant liquor-to-wood ratio of 7:1 is 1356 kg for an overall liquor-to-wood ratio of 13,56:1. Under these conditions the average sugar concentration in the combined residual aqueous phase (271 kg) is 30% (82,3 kg of recovered sugars).

In continuous percolation, the liquor-to-wood ratio can be kept constant at 10:1 as by necessity successive additions both wood and liquor will carry hydrolyzates of the residuals already within the reactor. This also establishes sugar concentrations to be in the order of 37 to 40% following flash evaporation of the volatiles. Such high sugar solids concentrations were hitherto possible only with strong acid hydrolysis systems but not with dilute acid hydrolysis.

Discussion of the liquor to wood ratio is extremely important in organosolv and acid hydrolysis processes since it directly relates to energy inputs during the hydrolysis and solvent recovery as well as during alcohol recovery from the resulting aqueous solution following fermentation of the sugars to ethanol or other organic solvents. Thus the liquor to wood ratio will have a profound effect on the economics of biomass conversion to liquid chemicals as well as the energy efficiency (energy gained over energy expanded in conversion) of the process.

Steaming of the comminuted cellulosic material before mixing with the hydrolysis liquor can be used to advantage to expel trapped air. Such treatment will aid rapid liquor penetration. Such practice is well known from the prior art.

Example I

Saccharification power and sugar survival were compared for three competitive systems namely: acidified water (aqueous weak acid), acidified aqueous ethanol and acidified aqueous acetone in the following example.

In every case purified cotton linters having TAPPI 0.5 percent viscosity of 35 cP and 73 percent crystallinity index at 7 percent moisture content were used. Acidification was affected with sulfuric acid by making up stock solutions of the various solvent systems each being 0.04 Normal with respect to the acid. Hydrolysis conditions were as follows:

In a series of experiments one gram samples of cotton linters (oven dry weight) were placed in glass lined stainless steel vessels of 20 ml capacity along with 10 ml of the solvent mixture and heated at 180°C for various lengths of time and residual solids and detected sugars in solution were plotted on graph paper. The times to obtain dissolution of about 99, 75, 50 and 25 percent of the substrate were read from the graphs and shown in Table 1. At the end of the reaction periods heating was interrupted, the vessel chilled and its cold contents filtered through medium porosity glass crucible, the undissolved residue first washed with warm water followed by rinsing with several 5 ml portions of acetone and finally by warm water. The residue weight was determined gravimetrically after drying at 105°C.

For comparative analytical purposes the combined filtrates were diluted to 100 ml with water and a half milliliter aliquot was placed in a test tube with 3 ml of 2.0 Normal sulfuric acid added and subjected to a secondary hydrolysis at 100°C by heating in a boiling water bath for 40 minutes. The solution was neutralized on cooling and the sugars present in the solution were determined by their reducing power. The results were thus uniform based essentially on the resultant monosaccharides liberated during the hydrolysis process. Theoretical percentage of reducing sugars available after the hydrolysis of the substrate was determined by difference between the known chemical composition of the starting material and the weight loss incurred due to the hydrolysis. To account for the weight increase of the carbohydrate fraction due to hydration of the polymer on breakdown into monomeric sugars, the weight loss is normally multiplied by 1.1111, the weight percentage (11.11%) of the added water to the cellulose in hydrolysis to monomeric sugars.

As evidenced from Table I, hydrolysis rates improved constantly as the acetone concentration increased to 50 percent. However, significant improvements were observed only as the acetone concentration was raised above 70 percent by volume of the acidified solvent mixture. Very rapid hydrolysis rates were obtained with nearly anhydrous acetone solutions. The dissolved sugars were found to be most stable when using a solvent mixture of between 80 to 90 percent acetone even though the relative half lives were relatively short. Sugar survivals over 90 percent are obtained as long as the reaction time at temperature is kept below that required for hydrolyzing 50 percent of the substrate to dissolved products. The time required to hydrolyze 50 percent of the substrate to dissolved products is called half life of sugar survival. This criteria holds regardless of what stage of hydrolysis is considered. The solvent effect both on the hydrolysis rate and sugar survival for limited hydrolysis times was the most surprising discovery of the present invention whereby maxima were found around 80 to 90 percent acetone concentration in the reaction mixture. At higher acetone concentrations, the response of the hydrolysis rate to increase in temperature and acid concentration was observed to follow well known kinetic principles in contrast to both the aqueous dilute acid and acidified aqueous ethanol systems in which the balance of increase in higher hydrolysis rates and sugar degradation did not improve with an increase in these parameters especially that of the temperature. The improved sugar survival with increase in acetone concentration is attributed to formation of acetone sugar complexes which have improved stability at high temperature. The complexes are very readily and safely hydrolyzable to free sugars on heating with dilute acid at 100°C for a limited amount of time.

In identical stationary acidified ethanol-water cooks, in which the ethanol concentration was higher than 80 percent neither delignification nor hydrolysis was obtained due to the fact that the acid catalyst was quickly consumed by reaction with the alcohol by formation of ethyl hydrogen sulfate ($C_2H_5—O—SO_2—OH$) and formation of diethyl ether via condensation of two ethanol molecules. Ether formation was quite substantial under these conditions. Also alkyl glucosides formed in high concentration alcohol solutions are substantially more difficult to hydrolyse to free sugars than the corresponding acetone complexes, and alcoholysis results in oligomeric sugars rather than monomers as is the case in acetone-water solutions. Thus alcohols prove to be largely unsuited for hydrolysis media due to the unwanted solvent loss and general danger from the explosive ether. With lignified materials the low delignification power of acidified alcohol solutions is clearly a drawback. With 80:20 ethanol:water cooks in the presence of 0.190 percent (0.04 Normal) sulfuric acid at 180°C the hydrolysis rate was 5.47×10^3 min^{-1} and the half life of cotton linters decomposition was 126.8 minutes. A maximum of 76 percent could be dissolved in 254 minutes, the crystalline residue showing substantial resistance to hydrolysis in the alcoholic solvent. Residual acid concentration was found to be one fourth of that originally applied, i.e., 0.01 Normal, the balance possibly consumed in the various side reactions.

It is evident from the data that under identical hydrolysis conditions excessively long hydrolysis times are required for complete dissolution of cotton linters both by acidified water and acidified aqueous ethanol media. An increase of the ethanol concentration from 50 percent to 80 percent did not improve the hydrolysis rate or improve particularly the sugar survival. The hydrolysis rate in ethanol water was only marginally better than in dilute acid in water.

These examples clearly show that a high acetone concentration over 70 percent is mandatory for high speed hydrolysis and high sugar survival. Under the conditions indicated for sugar recoveries better than 90 percent, reaction times (or high temperature exposure times of less than indicated for half lives are preferred). Thus according to these data, total saccharification and quantitative sugar recovery would dictate a percolation or pass through process wherein the liquor residence time would not exceed 10 minutes when 80:20 acetone:water with 0.04 Normal sulfuric acid is used as solvent mixture at 180°C temperature. The residence time would have to be substantially shortened when higher temperatures and larger acid concentrations are used as shown in the following examples.

Solid residues less than 50% in yield show high degree of crystallinity (87%) and are pure white, have a DP (degree of polymerization) of 130 to 350.

TABLE 1

Forward reaction rates in stationary hydrolysis of cotton linters as a function of acetone concentration

Catalyst: 0.04 N H_2SO_4; Temp. 180°C,
Liquor/wood=10/1.

Acetone/ water ratio	Dissolved cellulose %	Reaction time min	R_x Rate 10^3 min^{-1}	Factor	Reducing sugar yield, %
0, H_2O	25	137	2.1	1	82
	50	330			46
	75	660			16
	99	2192			—
10/90	25	115	2.5	1.2	— Too slow hydrolysis rate and generally poor sugar recoveries.
	50	277			—
	75	555			—
	99	1842			—
30/70	25	91	3.16	1.5	—
	50	219			—
	75	439			—
	99	1458			—
50/50	25	49	5.89	2.8	95 Exc. Recov.
	50	118			64 Good Recov.
	75	235			36 Poor
	99	783			27 Recovery
70/30	25	12	24.1	11.5	98 Exc. Recov.
	50	29			73 Good Recov.
	75	58			45 Poor
	99	191			35 Recovery
80/20	25	5	52.7	25.1	99 Excellent
	50	13			96 Recovery
	75	26			73 Good Recov.
	99	87			58 Poor Recov.
90/10	25	3	112.8	53.7	99 Excellent
	50	6			94 Recovery
	75	12			79 Good Recov.
	99	41			56 Poor Recov.

Example II

The effect of acid concentration on the rate of hydrolysis and sugar survival in 80:20 acetone:water solvent mixtures was studied at 180°C temperature using cotton linters as substrate.

In stationary cooks one gram samples (oven dry) of cotton linters were hydrolyzed in glass lined stainless steel pressure vessels along with 10 ml of the appropriate hydrolysis liquor and heated until the original substrate mass was hydrolyzed and dissolved. The levels of 25, 50, 75 and 99 percent of hydrolysis were determined by graphing as in Example I.

Work-up of the reaction products followed the same procedure as outlined in Example I. The results are indicated in Table 2.

Increased acid concentration resulted in higher hydrolysis rates within the range studied and a somewhat faster degradation of the sugars as the single stage hydrolysis times exceeded those indicated as half lives for the solid residue. Equal concentrations of sulfuric and hydrochloric acid were found to give largely comparable results. The increased acid concentrations showed a substantial hydrolysis accelerating effect as evidenced by the rapidly decreasing half lives. Thus the hydrolysis rate can be readily controlled by limited acid concentrations, all other conditions being held constant.

TABLE 2

Effect of acid concentration on forward hydrolysis rates in stationary hydrolysis of cotton linters
Temp.: 180°C, Solvent:Acetone/Water=80/20, L/W−10/1.

Acid conc. normal	H_2SO_4 %	Dissolved cellulose %	Reaction time min	R_x Rate 10^3 min^{-1}	Factor	Reducing sugars %
0.01	0.047	25	32.3	8.9	1	99
		50	77.9			90
		75	155.8			67
		99	517.0			57
0.02	0.095	25	12.2	23.6	2.65	99
		50	29.4			95
		75	58.8			71
		99	195.0			67
0.04	0.190	25	5.0	52.7	5.92	99
		50	13.0			96
		75	26.0			73
		99	87.7			58
0.06	0.285	25	3.5	82.0	9.2	99
		50	8.5			87
		75	17.0			63
		99	56.2			52
0.10	0.475	25	2.3	123.8	13.9	99
		50	5.6			88
		75	11.2			60
		99	37.3			50
0.02 HCl	0.07	25	12.8	21.7	2.44	98
		50	30.1			92
		75	61.2			69
		99	204.3			60

Example III

Temperature effects on hydrolysis of cotton linters were studied with acidified aqueous acetone solutions containing 0.04 Normal sulfuric acid in 80:20 acetone:water at different hydrolysis times so that weight losses of 25, 50, 75 and 99 percent could be determined as in Example I. All cooks were preconditioned to 35°C before being placed in the oil bath to minimize the effect of heating-up time at the various temperature levels studied.

Work-up of the products and analysis followed the same procedure as described in Example I and the results are summarized in Table 3.

The data indicate that increased temperature had the most profound accelerating effect of the hydrolysis rate and generally in such single stage batch cooks reaction times exceeding sugar dissolution half lives at any stage of the hydrolysis increased somewhat the rate of sugar degradation at the higher temperature regimes used. However, it was learned that such high temperature hydrolyses afford practically instantaneous high-yield hydrolysis to be carried out on even such difficult to hydrolyze substrate as cotton linters. The rate of sugar degradation can be offset somewhat by lowering the acid concentration and by increasing the liquor to wood ratio whereby the forward reaction rate (k_1) in hydrolysis remains unaffected but the sugar degradation rate (k_2) is lowered. Thereby sugar survival, which depends on the ratio of k_1/k_2 is largely improved especially if high acetone concentrations are used.

TABLE 3

Effect of temperature on hydrolysis rate of cotton linters and survival of sugars in acidified 80:20 acetone water.
Catalyst: 0.04 Normal H_2SO_4, L/W=10/1.

Reaction temp. °C	Dissolved cellulose %	Reaction time min	R_x Rate 10^3 min^{-1}	Factor**	Reducing sugars %
145*	25	40	7.2	3.42	78
	50	96			65
	75	193			53
	99	640			40
160	25	19	21.6	10.3	91
	50	49			64
	75	98			48
	99	329			37
180	25	5	52.7	25.1	99
	50	13			96
	75	26			73
	99	87.7			58
200	25	1.0	301	143	99
	50	2.3			98
	75	4.6			78
	99	15.2			63
210	25	0.39	745	354	99
	50	0.93			92
	75	1.86			80
	99	6.17			58

* Acetone/water=90:10, 0.10 Normal H_2SO_4

** k_{water}=1.0 (k_1=2.1; Table 1)

Example IV

Cooks reported in this example explore the hitherto unobserved relationship of increasing the sugar survival at reduced acid concentration and increased reaction temperatures without any reduction in the high hydrolysis rates disclosed herein. This unusual discovery is demonstrated in the data of Table 4.

The effect of reduced acid concentration but high reaction temperature is demonstrated by cooking one gram samples of cotton linters (oven-dry weight) in glass lined stainless steel pressure vessels along with 10 ml of 80:20 acetone:water cooking liquor containing 0.01 and 0.005 Normal H_2SO_4 with respect to the solvent mixture, and heated until 50 percent and 75 percent dissolution of the substrate was obtained at 190 to 220°C reaction temperature.

Cooling and work-up of the reaction products to determine sugar survival and reaction rates were performed as outlined in Example I.

The data indicate that acid concentration can be successfully reduced and traded by increasing the reaction temperature without loss in reaction rate with a concomittant increase in sugar yield (survival) when hydrolysis liquors of at least 80 percent acetone content are used. Such a trend is clearly against all previously published scientific results (Seamen, J.F., ACS, Honolulu 1979; Bio-Energy, Atlanta 1980) where the increase in hydrolysis rates and sugar survival was a function of both increased acid concentration and higher temperature. The surprising solvent effect of the acetone water system has never been observed or reported in scientific literature or the prior art before.

TABLE 4

Effect of high reaction temperature and very low acid catalyst concentration on survival of sugars on hydrolysis of cotton linters in 80:20 Acetone:Water solvent.
L/W=10/1.

Reaction temp. °C	Dissolved cellulose %	Reaction time min	R_x Rate 10^3 min^{-1}	Reducing sugars %
0.01 Normal $[H_2SO_4]$ 490 ppm				
180	50	48.1	14.4	87.7
	75	96.3		64.8
190	50	18.8	36.8	90.4
	75	87.7		70.5
200	50	7.4	94.2	91.5
	75	14.8		73.2
210	50	2.0	241.4	91.5
	75	5.7		75.7
0.005 Normal $[H_2SO_4]$ 245 ppm				
190	50	45.3	15.3	92.0
	75	90.6		73.3
200	50	17.7	39.2	93.0
	75	35.5		74.4
210	50	6.9	100.4	94.0
	75	13.8		78.4
220	50	2.7	257.8	96.3
	75	5.4		81.0
230	50	0.25	659.9	98.0
	75	0.36		87.5

Example V

One gram samples of several wood species were hydrolyzed in 80:20 acetone:water containing 0.04 Normal sulfuric acid at 180°C. Hydrolysis rates were calculated only for the crystalline cellulose fractions to avoid the confounding effect of easily hydrolyzable lignin and hemicelluloses. Times to mass losses of 25, 50, 75 and 99 percent of the original oven dry mass along with the calculated reaction rates are recorded in Table 4.

Work-up of the products followed the same procedure as indicated in Example I except that after removal of the volatiles by distillation it was necessary to remove the precipitated lignins by filtration or centrifuging.

It is quite evident that under identical conditions the hydrolysis rates for wood are roughly twice that of cotton linters. Due to the increased forward reaction rates sugar recoveries became quite impressive indeed.

The rate of Douglas-fir hydrolysis was somewhat slower than that of aspen and sugarcane rind. However, when hydrolysis in a purely aqueous system was attempted under otherwise exactly matching conditions (same temperature and acid catalyst content) a hydrolysis rate of 0.5×10^3 min^{-1} was obtained and only 6 percent weight loss was recorded for a 280 min long cook at 180°C the usual dilute acid hydrolysis temperature. Thus the high acetone content hydrolysis liquor allowed at least 100 times faster hydrolysis of Douglas fir by simultaneous dissolution of the lignin than possible in purely aqueous systems.

Among the products of partial saccharification of wood, solid residues of about 30 to 35% yield are pure white, devoid of residual lignin. This cellulosic fraction has a crystallinity index of 80% from aspen wood and a degree of polymerization (DP) of between 80 to 280. Similar results are obtained with the other wood species.

TABLE 5

Hydrolysis rates of selected wood species in 80:20 Acetone:Water mixtures at 180°C in the presence of 0.04 normal sulphuric acid as catalyst.
(Liquor/Wood=10/1)

Wood species	Dissolved cellulose, %	Reaction time, min	R_x Rate 10^3 min^{-1}	Factor	Reducing sugars, %
Aspen	25	2.1	135.2	—	99
	50	5.0			98
	75	10.3			96
	99	34.5			92
Sugarcane Rind	25	2.2	134	—	99
	50	5.0			98
	75	10.4			96
	99	34.5			92
Douglas-Fir	25	3.0	98	—	99
	50	7.0			97
	75	14.0			92
	99	46.1			86

Example VI

It is found to be a further advantage of the present invention that the high acetone concentration clearly favors formation of relatively stable acetone-sugar complexes in spite of the presence of water. The better stability of the sugar complexes at high temperature profoundly affects survival of the dissolved sugars. The improvements are quite evident from the data in Table 1.

Further due to the differences in volatility and solubility of the various sugar complexes the invention allows facile segregation and nearly quantitative isolation of the five major wood sugars, if so desired. However, due to the mixed nature of the sugar derivatives in aqueous hydrolyzates, if such thorough and detailed separation is desired, it is always necessary to neutralize the recovered aqueous sugar wort after removal of the volatiles and concentrate the wort to a syrup. The syrup is then redissolved in anhydrous acetone containing 3 percent acid, allowed to stand at least 6 hr until all sugars formed their respective di-acetone complexes before attempting the detailed separation as described below. The separated sugar complexes are readily hydrolyzed in dilute acid on boiling at least 20 to 40 minutes.

Thus 10 g (OD) coarse aspen wood sawdust (passing a 5 mesh screen) was charged with 100 ml of hydrolyzing liquor made up to 80:20 acetone:water and 0.04 Normal sulfuric acid as catalyst. The bomb was brought to 180°C temperature by immersing it into a hot glycerol bath within 9 min and heating was continued until the required reaction times were reached.

In another larger bomb 450 ml of hydrolysis liquor containing 80:20 acetone:water and 0.04 Normal sulfuric acid was also preheated and connected through a syphon tube and shut-off valve to the reaction vessel. Following three minutes at reaction temperature (9+3=12 min total) the reaction liquor was drained into a small beaker containing 75 g crushed ice. The reaction vessel was immediately recharged with hot liquor from the stand-by vessel and the reaction was allowed to proceed for an additional 3 minutes before again discharging the reactor contents as above. In all, five liquor changes were effected and the liquors collected for analysis. The chilled reactor contents were analyzed as follows:

Hydrolysate No. 1 and 2 were combined before evaporation of the low boiling volatiles. Flash evaporation of the acetone at low temperature (50°C) and reduced pressure resulted in precipitation of a flocculant lignin which aggregated to small clusters of granules on standing. The lignin was carefully filtered off the mother liquor, washed with two portions of water and dried *in vacuo* to constant weight as a powder. The lignin powder collected weighed 1.67 g and had a weight average molecular weight of 2800.

The combined filtrate (127 ml) was neutralized and subjected to steam distillation in an all glass apparatus and approximately 35 ml distillate was collected. Both the distillate and residual solution were made up to 100 ml and 0.5 ml portions of each were acidified with sulfuric acid to 3 percent acid and boiled for 40 min on a water bath. The solutions were neutralized and the sugar reducing power determined by the Somogyi method. The yield of sugars was 1.89 g in the distillate and 1.96 g from the residual liquor.

Gas chromatographic determination of alditol acetates of the sugars from the steam distillate indicated mainly xylose and arabinose whereas from the residual solution glucose, mannose and galactose with only minor traces of xylose were indicated.

Hydrolysate No. 3 contained only traces of lignin after evaporation of the acetone solvent too small to collect and determine gravimetrically. It was removed by centrifuging. The aqueous residue (97 ml) was acidified to 3 percent acid with sulfuric acid, boiled for 40 min and after neutralization filtered and made up to 100 ml. The reducing sugar content of the filtrate was determined by the Somogyi method to be 1.83 g. GC analysis of the alditol acetates determined on an aliquot sample indicated mainly glucose with traces of mannose and galactose.

Hydrolysate No. 4 and 5 were processed and analyzed in the same manner as No. 3. H-4 yielded 1.73 g reducing sugars and H-5 yielded 1.40 g sugars both being composed only of glucose as evidenced by GC analysis of an aliquot sample.

The undissolved residue was 0.12 g following 2 h drying in an oven at 105°C.

The recoveries summarize as follows:

Lignin powder	1.67 g
Total pentose sugars	1.89 g
Total hexose sugars	6.92 g
Undissolved residue (99% glucose)	0.12 g
	10.60 g

Mass Balance:

1. Lignin Recovery:	98.2%
2. Sugar Recovery:	97.8%

Example VII

In a similar hydrolysis arrangement to Example VI 10 g OD Douglas-fir sawdust (to pass a 10 mesh screen), pre-extracted with dichloromethane and air dried to 8 percent moisture content in a controlled humidity room, was hydrolyzed with 80:20 acetone:water solvent containing 0.05 Normal Hydrochloric acid in five consecutive steps. Each reaction step consisted of three minutes at a reaction temperature of 200°C. The heating up time was 7 minutes. Again Hydrolysate No. 1 and 2 were combined whereas the subsequent fractions were analyzed separately.

The combined liquor of H-1 and H-2 yielded 2.39 g lignin on low temperature evaporation of the volatiles and 135 ml of aqueous liquor was collected on filtration of the powdered lignin. The dried lignin had a weight average molecular weight of 3200. The filtrate was neutralized to pH 8 and subjected to steam distillation in all glass apparatus. The 28 ml distillate which was collected contained 0.62 g pentoses which after passing the filtrate through a cation exchange resin in the acid form and repeated steam distillation of the filtrate yielded 0.58 g xylose as determined by GC analysis.

The residue remaining behind after the above steam distillation (128 ml) was neutralized on an ion exchange column, the filtrate concentrated to a syrup, seeded with some crystalline mannose and left standing overnight. The crystalline material was collected by filtration and recrystallized from ethanol-petroleum ether. The crystals were re-dissolved in water, acidified to 3 percent acid and boiled for 40 min to liberate the free sugars. After neutralization with silver carbonate the solution was analyzed by GC alditol acetates to determine the sugar concentration. The only sugar detected by GC was mannose and the yield was calculated as 1.00 g.

The ethanol-petroleum ether solution was extracted with 5 ml portions of water and the collected aqueous layer combined with the syrup removed from the crystalline product above. The solution was briefly heated to expel the alcohol, made up to 3 percent acid with hydrochloric acid, boiled for 40 min, neutralized with silver carbonate and alditol acetates were prepared for GC analysis. The combined syrup and filtrate contained a total of 58 g sugars of which 0.29 g was galactose, 0.25 g was glucose and 0.04 g was mannose.

Hydrolysate No. 3 gave 1.89 g pure glucose with 0.4 g of lignin precipitate on removal of the volatiles.

Hydrolysate No. 4 gave 1.66 g of pure glucose with only very small traces of lignin, whereas H-5 gave 1.85 g of glucose and no lignin. The undissolved residue was 0.18 g and was composed of 99 percent glucose.

The recoveries summarize as follows:

H-1, 2&3:	Lignin	2.79 g
	Xylose	0.58 g
	Arabinose (by difference)	0.04 g
	Mannose	1.00 g
	Hexoses	0.58 g
H-3:	Hexoses	1.89 g
H-4:	Hexoses	1.66 g
H-5:	Hexoses	1.85 g
	Unhydrolyzed residue	0.18 g
		10.57 g

Total Sugar Recovery: 7.60 g=95.95% (of theoretical)
Lignin Recovery: 98%

Under large scale industrial conditions chilling of the recovered sugar solutions is best accomplished by controlled flash evaporation of the volatiles. Cooling of the liquor samples outside of the pressure vessel in Examples VI and VII with crushed ice was adapted as matter of convenience for small scale treatments.

Claims

1. A process for the production of sugars from particulate cellulosic material by treating the material in a pressure vessel with a cooking liquor consisting of acetone and water and containing an acidic compound in a concentration of from 0.001 to 0.1 N at a temperature of from 145°C to 230°C, wherein:

a) the mixture of acetone and water has an acetone concentration of greater than 70 volume-%,

b) the cooking liquor and particulate cellulose material are introduced into the pressure vessel at such a rate that the time elapsing between feeding and exit of the products does not exceed that determined earlier to obtain 50% hydrolysis of the solids,

c) the product solution is rapidly cooled to under 100°C to avoid degradation of the sugars such that at least 90% of the solubilized sugars are recovered.

2. A process as claimed in claim 1, wherein the cellulosic material comprises lignocellulosic material and the cooking product solution is rapidly cooled by flash-evaporation of the acetone from the solution of sugars and lignin at 50°C to precipitate the lignin.

3. A process according to claim 1 or 2, wherein the mixture of acetone and water has an acetone concentration of 80 to 90 volume-%.

4. A process according to claim 1, wherein the ratio of liquor to cellulosic or lignocellulosic material is 7:1 to 10:1.

Patentansprüche

1. Verfahren zur Gewinnung von Zuckern aus feinteiligem cellulosischem Material durch Behandeln des Materials in einem Druckbehälter mit einer Kochflüssigkeit, die aus Aceton und Wasser besteht und eine saure Verbindung in einer Konzentration von 0.001 bis 0.1 N enthält, bei einer Temperatur von 145 bis 230°C, wobei

a) das Gemisch von Aceton und Wasser eine Acetonkonzentration von über 70 Volum-% hat,

b) die Kochflüssigkeit und das feinteilige Cellulosematerial mit einer solchen Geschwindigkeit in den Druckbehälter eingebracht wird, daß die Zeit, die zwischen Beschickung und Austritt der Produkte verstreicht, die gemäß vorheriger Bestimmung für die Hydrolyse von 50% der Feststoffe erforderlich ist, nicht übersteigt,

c) die Produktlösung rasch auf unter 100°C gekühlt wird, um den Abbau der Zucker zu verhindern, so daß wenigstens 90% der gelösten Zucker gewonnen werden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das cellulosische Material lignocellulosisches Material ist und die Produktlösung durch Entspannungsabdampfen des Acetons aus der Lösung von Zuckern und Lignin rasch auf 50°C gekühlt wird, um das Lignin auszufällen.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Gemisch von Wasser und Aceton ein Acetonkonzentration von 80 bis 90 Volum-% hat.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Verhältnis Flüssigkeit zu cellulosischem oder lignocellulosischem Material 7:1 bis 10:1 beträgt.

Revendications

1. Procédé de production de sucres à partir d'une matière cellulosique en particules par traitement de la matière dans un récipient sous pression avec une liqueur de cuisson consistant en acétone et eau et contenant un composé acide à une concentration de 0.001 à 0.1 N à une température de 145 à 230°C, dans lequel:

a) le mélange d'acétone et d'eau a une concentration en acétone supérieure à 70% en volume,

b) la liqueur de cuisson et la matière cellulosique en particules sont introduites dans la récipient sous pression à une vitesse choisie de manière que le temps écoulé entre l'alimentation et la sortie des produits n'excède pas le temps déterminé précédemment pour obtenir l'hydrolyse à 50% des matières solides,

c) la solution du produit est rapidement refroidie au-dessous de 100°C pour éviter la dégradation des sucres, de manière à recueillir au moins 90% des sucres solubilisés.

2. Procédé suivant la revendication 1, dans lequel la matière cellulosique comprend une matière lignocellulosique et la solution de produit de cuisson est refroidie rapidement par évaporation instanée de l'acétone de la solution de sucres et de lignine à 50°C pour précipiter la lignine.

3. Procédé suivant la revendication 1 ou 2, dans lequel le mélange d'acétone et d'eau a une concentration en acétone de 80 à 90% en volume.

4. Procédé suivant la revendication 1, dans lequel le rapport de la liqueur à la matière cellulosique ou lignocellulosique est de 7:1 à 10:1.