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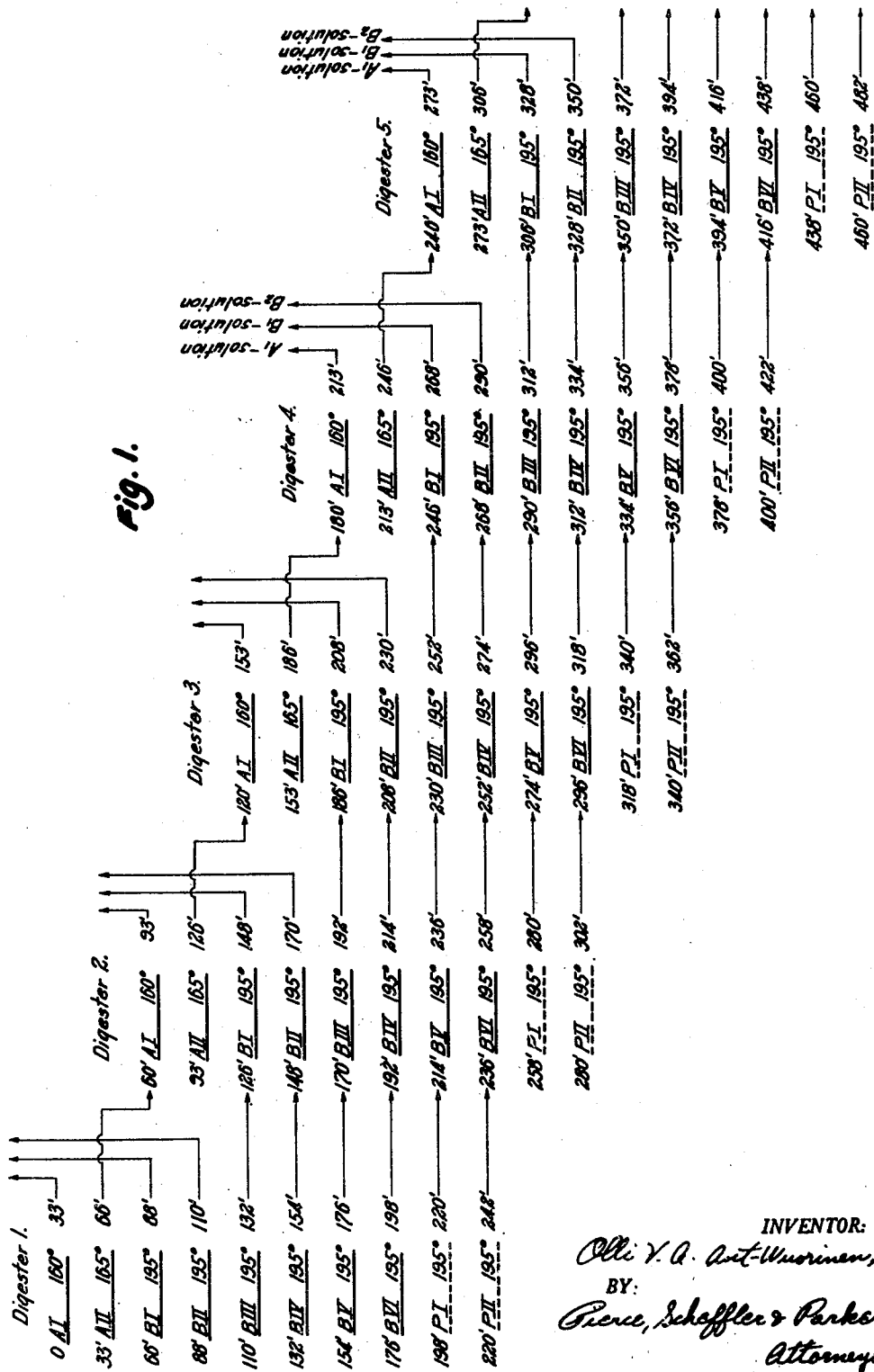
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2,516,833

PROCESS FOR HYDROLYZING CELLULOSIC MATERIALS

Filed July 17, 1947

2 Sheets-Sheet 1



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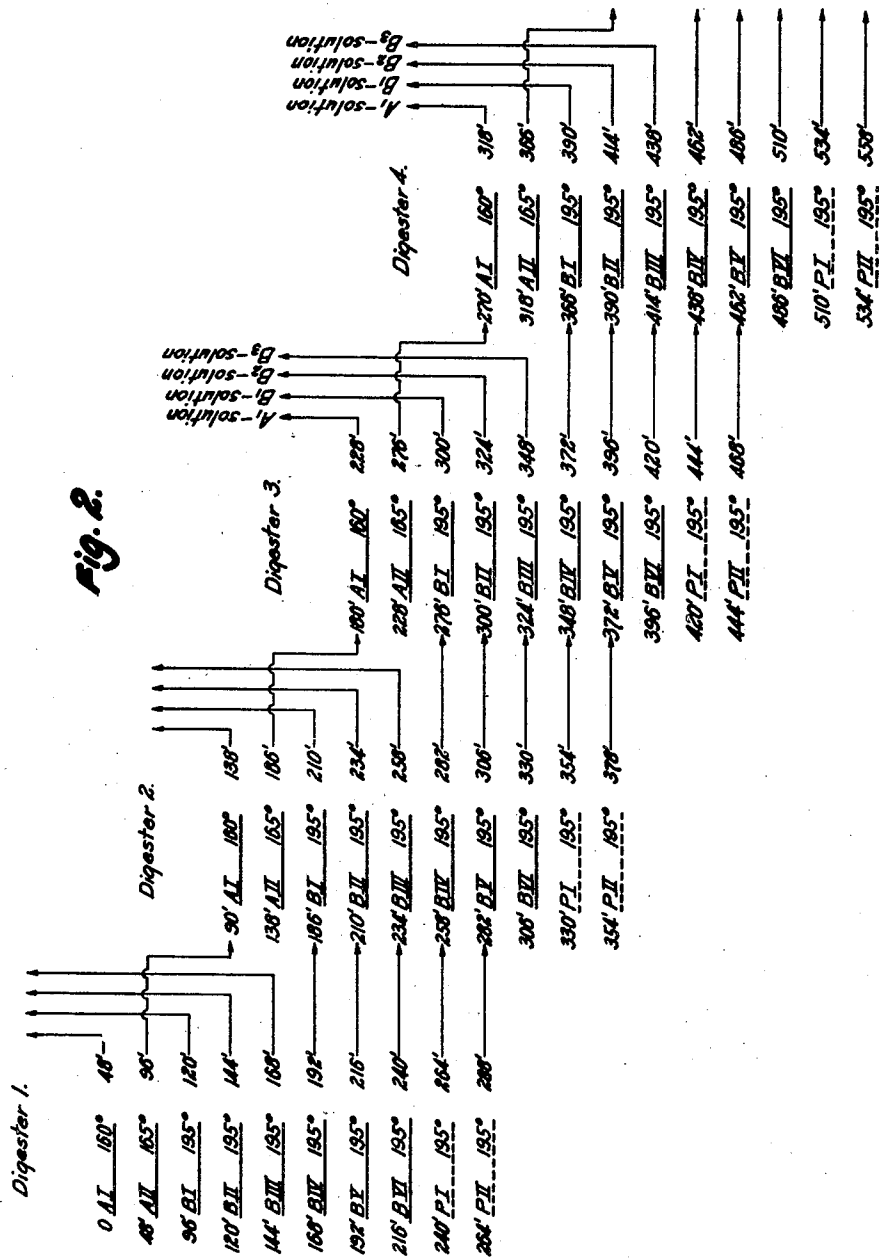
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UNITED STATES PATENT OFFICE

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PROCESS FOR HYDROLYZING CELLULOSIC MATERIALS

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13 Claims. (Cl. 127—37)

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This invention relates to the hydrolyzing of the carbohydrate part of wood or other cellulose materials with dilute acid solutions.

Numerous different processes exist for hydrolyzing the carbohydrate part of wood with dilute acid solutions. In some processes many successive batches of hydrolyzing liquid are allowed to react with the wood contained in a digester while in other prior known methods acid solutions regulated in a specific manner are continuously forced through the digester, e. g. Swedish Patents Nos. 105,420, 107,869, 107,933, 107,934, and 108,126 relate to a process of saccharification of wood wherein successive batches of acid solutions are used and effectively circulated in the digester during each saccharification phase.

Also other processes are known wherein higher concentration of sugar in solutions obtained as hydrolysis product are aimed at by flowing the formed sugar solution, according to the generally known countercurrent principle, into fresher wood than that with which it has previously reacted in the next digester of the used series of digesters. The present invention has for its object the arrangement of wood hydrolysis in such a way that simultaneously as the sugar solution containing sugars extracted from the hemicellulose part of wood is separated as quantitatively as possible from that composed of sugars originating from the cellulose part of wood, the sugar concentration of both types of sugar solutions is raised as high as possible.

The invention makes possible the commercial production of crystalline hexose sugars by means of hydrolysis of the cellulose part of wood in a process involving separate production and treatment of pentose and hexose sugar fractions from the respective hemicellulose and cellulose parts of the wood and further involving the use of (a) dilute solutions of SO_2 (not exceeding 2.0% SO_2 by weight) as the hydrolyzing liquid, (b) circulation of the acid within the digesters, (c) contact of successive batches of hydrolyzing liquid with a given digester charge, (d) countercurrent flow of the solution formed, and (e) maintenance of proper temperatures (preferably 155°–165° C. for hydrolysis of the hemicellulose and preferably 180°–205° C. for hydrolysis of the cellulose).

In carrying out the process of the present invention the sugar solution containing sugars originated from hemicellulose is concentrated separately by flowing said solution in a series of a plurality of digesters from one digester to another and separately in like manner the sugars

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originating from the cellulose part of wood, i. e. the sugar solution containing hexose sugars for the major part. This is achieved by treating the wood to be hydrolyzed with several successive batches of hydrolyzing liquids, these several successive treatments being hereinafter termed "hydrolysis stage." At least two of these hydrolysis stages, the number of which can vary, are carried out at a temperature below 170° C., preferably at a temperature in the range of 155°–165° C. (called in the following, A-stages) and the others at a temperature exceeding 170° C., preferably within the range 180°–205° C. (called B-stages in the following). In addition to these it is advisable, though not necessary, to wash the solid lignin residue in the digester once or several times with hot water (these washwater batches are termed wash stages in the following).

When using dilute hydrolyzing liquids, i. e. those containing under 2 per cent and preferably not under 0.2 per cent of hydrolyzing agent, at the temperature range of 155°–165° C. the velocity of hemicellulose hydrolysis is much greater than the velocity of decomposition of the monosaccharides formed as hydrolysis products. Again at the temperature range of 185°–205° C. the velocity of cellulose hydrolysis exceeds the velocity of the decomposition of the monosaccharides formed as hydrolysis products. Moreover, the velocity of cellulose hydrolysis below 170° C. is so low that only negligible amounts of cellulose hydrolyze in the A-stages wherefore the sugar solution obtained as a product in the B-stages for the major part contains hexose sugars and only a few per cent of pentose sugars chiefly formed from hemicellulose, the pentose sugars thus concentrating for the major part in the solution from the A-stages.

On connecting, by means of pipe lines and valves, several of the digesters in series it is possible to have the same batch of hydrolyzing liquid react in a hydrolyzing manner with more than one batch of wood to be hydrolyzed and thus to obtain a higher concentration of sugar. This concentration yields best results when using aqueous solutions of sulfur dioxide (SO_2) as hydrolyzing liquids.

The different hydrolysis stages of different digesters are interconnected in such a way that from each digester is withdrawn a total of two, three or four batches of product sugar solution, the first withdrawn solution—hereinafter termed an A-solution—thus consisting of the hydrolysis solution formed in successive A-phases and containing sugars originating from the hemicellulose

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part of wood. On the other hand the sugars originating from the cellulose part are contained in one, two or three sugar solution batches withdrawn after the A-solution and hereinafter termed B-solutions. The B-solutions have been formed from the hydrolysis liquid batches reacting in separate digesters at B-stages. If there are two or three B-solutions per digester they are referred to as B₁- and B₂- or B₁-, B₂-, and B₃- solutions.

Experiments carried out have shown that it is not economical to combine all the sugars originating from the cellulose part into the one and same withdrawn batch nor to increase the number of B-solutions to more than three, so that in the following examples only those cases having two or three B-solutions to a digester are referred to.

The various features of novelty which characterize my invention are pointed out with particularity in the claims annexed to and forming a part of this specification. For a better understanding of the invention, its operating advantages and specific objects attained by its use, reference should be had to the accompanying drawings illustrative of the invention and in which: Fig. 1 is a flowsheet of a system for carrying out a process embodying the invention, and Fig. 2 is a flowsheet of a similar system for carrying out a form of the process of the invention modified from that illustrated in Fig. 1. The invention will be more fully described in the following two examples based on Fig. 1 and Fig. 2, respectively.

Example 1.—Hydrolysis carried out in accordance with the concentration diagram of Fig. 1 requires six digesters designated by the numerals 1-6 by means of which 24 digesters full of wood are hydrolyzed in 24 hours, i. e. four cycles to each digester in 24 hours. Water preheated to the temperature desired is introduced into the digester series and the requisite amount of liquid SO₂ is added at the appropriate time as indicated below, e. g. by use of overpressure created by means of an air compressor, to the digesters designated by numerals 1-6 the liquid content of which is kept in lively circulation, e. g. by means of a centrifugal pump and circulation pipe lines during the duration of each hydrolysis stage. The liquid used in each phase of treatment can be either transferred to any other digester desired or withdrawn from said digester, e. g. through a heat exchanger.

There is a total of three withdrawn batches of product solution per digester, i. e. the A-solution and the B₁- and B₂- solutions.

In the diagram the horizontal full lines designate the hydrolysis stages which, in this example, consist of two A-stages and six B-stages, while the horizontal dash lines stand for wash stages numbering two. The diagram illustrates the starting phase of the system up to digester 4 which is the first to yield solutions that have attained the sugar concentration aimed at. On the left hand side of the line illustrating the treatment stage the time indicating the beginning of the stage is shown and on the right hand side of the same line the time for completion of the stage, both calculated in minutes from the moment 0 when the system is started.

Fresh water or wash water is added to all the stages which are not supplied, as indicated by arrows, with the hydrolyzing liquid which has already reacted in the previous digester. The treatment stage is calculated to begin at that moment when either hot fresh water or hydrolyzing liquid which has reacted already in some

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other previous digester is started to be introduced into the treating digester and is calculated to end at that moment when the freely moving liquid portion of said treating digester contents has been withdrawn either by utilizing overpressure or/and pump, at which said liquid is simultaneously transferred to a subsequent digester or/and removed from the system as a ready sugar solution. The digester and the sieve plates, circulation pipe lines, and corresponding pump are so dimensioned that said digester can be filled with and emptied of the freely moving liquid in six minutes. Accordingly, when the aforementioned liquid content of the digester is being transferred to another digester of the series the treatment stage of the digester to which transference is being made is calculated to begin six minutes before the end of the treatment stage in the digester from which transference is being made.

In the diagram the hydrolysis stages are indicated with AI—AII and BI—BVI and the wash stages with PI—PII. In this example, the hydrolyzing agent employed was an aqueous solution of SO₂, containing 0.7 per cent SO₂ by weight. Also the temperature of each treatment stage can be had from the diagram. The temperature can be maintained at the point desired by e. g. introducing high pressure fresh steam into the digesters.

Examination of the diagram will show that a digester full of wood is hydrolyzed to the end and the solid hydrolysis residue, i. e. lignin is washed twice in a total of 242 minutes (=4 hrs. 2 min.) and in a series of six digesters (since a new digester filled with fresh wood is coupled to the system every 60th minute) digester 1 is employed again after removal of lignin, filling with fresh wood and presteaming within 6 hrs. (=360 min.) from the initial moment 0. For these intermediate procedures the hour and 58 minutes at hand is quite sufficient.

On hydrolyzing according to the example described above a yield of 55-60 per cent of reducing sugar in relation to dry wood weight is obtained. When the filling density of the digester is about 200 kilograms of fir wood calculated dry per cbm. digester the average sugar content of the A-solution is 9-10 per cent, that of B₁- and B₂-solutions 6.5-7.0 per cent, and the average sugar content of all three solutions about 7.5-8.0 per cent. Simultaneously the sugar obtained in the B-solutions forms about 55 per cent of the total sugar yield and the hexose content thereof exceeds 95 per cent.

Example 2.—When hydrolyzing according to the concentration diagram of Fig. 2 five digesters are necessary with which 16 digesters full of wood are hydrolyzed in 24 hours, in other words a little over three digester fills of wood to each digester in 24 hours. Fresh water preheated to the temperature desired is introduced into the digester series and thereafter the same procedure is followed as described in Example 1.

There are four withdrawals from the system of product solution per digester, i. e. the A-solution and the B₁-, B₂-, and B₃-solutions.

In the diagram the full lines designate the hydrolysis stages, which in this example consist of two A-stages and six B-stages, and the horizontal dash lines represent wash-stages numbering two. The diagram illustrates the starting phase of the system up to the third digester which is the first to yield solutions that have attained the sugar concentration aimed at. On the left hand side of the line illustrating the treatment stage the time indicating the begin-

ning of the stage is shown and on the right hand side of the same line the time for completion of the stage, both calculated in minutes from the moment 0 when the system is started. Fresh water or wash water is added to all the stages which are not supplied, as indicated by arrows, with hydrolyzing liquid which has already reacted in the previous digester. The treatment stage is calculated to begin at the moment when either hot fresh water or hydrolyzing liquid which has already reacted in some previous digester is started to be introduced into the treating digester and is calculated to end at that moment when the freely moving liquid portion of said treating digester contents has been withdrawn either by utilizing overpressure or/and pump, at which said liquid is simultaneously transferred to the next digester or/and removed from the system as a ready sugar solution. The digester and the sieve plates, circulation pipe lines and corresponding pump are so dimensioned that the digester can be filled with and emptied of the freely moving liquid in six minutes. Accordingly, when the aforementioned liquid content of the digester is being transferred to another digester of the series the treatment stage of the digester to which transference is being made is calculated to begin six minutes before the treatment stage in the digester from which transference is being made ends.

In the diagram of Fig. 2 the hydrolysis stages are indicated with AI—AII and BI—BVI and the washstages with PI—PII. In this example, the hydrolyzing liquid is an aqueous solution of SO_2 , containing about 0.7 per cent SO_2 by weight. Also the temperature of each stage can be had from the diagram. The temperature can be maintained at the point desired by e. g. introducing high pressure fresh steam into the digesters.

Examination of the diagram will show that a digester full of wood is hydrolyzed to the end and the solid hydrolysis residue, i. e. lignin, is washed twice in a total of 288 minutes (=4 hrs. 48 min.) and that in a series of five digesters—since a new digester filled with fresh wood is coupled to the system every 90th minute—digester I is employed again, after removal of lignin, filling with fresh wood and presteaming within 7 hrs. 30 min. (=450 min.) from the initial moment 0. For these intermediate procedures the 2 hrs. 42 min. at hand are quite sufficient.

On hydrolyzing according to the example described above a yield of 57–62 per cent of reducing sugar in relation to dry wood weight is obtained. When the filling density of the digester is about 200 kilograms of fir wood calculated dry per cbm. digester the average sugar concentration of the A-solution is 9–10 per cent, that of B₁-, B₂-, and B₃-solutions about 4.5–5.5 per cent and the average sugar content of all four solutions about 6–7 per cent. Simultaneously the sugar content of the B-solutions is over 55 per cent of the total sugar yield and the hexose content thereof over 95 per cent.

While in accordance with the provisions of the statutes I have illustrated and described herein some forms of the invention now known to me, those skilled in the art will understand that changes may be made without departing from the spirit of the invention covered by my claims, and that certain features of the invention may sometimes be used to advantage without a corresponding use of other features.

In addition to the technical and economical advantages achieved by means of this novel ar-

rangement of hydrolysis, mention is made of the facts that the utilization ratio is high and in spite of the high sugar yield the average sugar content of the solutions is also of the highest grade possible and further (practice has shown) that more than half of the total sugar yield (B-solutions) obtained is so pure a glucose solution that said solution can be evaporated as such after neutralization and used for the manufacture of pure crystalline glucose. The sugar solution containing the monosaccharides originating from the total carbohydrate part of wood (as e. g. the mixture of A- and B-solutions) is unfit for the technical manufacture of glucose. Moreover, the sugar content of the B-solutions in question is so high that evaporation costs keep within reasonable bounds.

I claim:

While it is not intended that the invention be limited to any particular theory, since it has not been determined to what factor or combination of factors the success of the process in efficiently producing a high content pentose sugar fraction and a separate hexose sugar fraction suitable for crystallization may be attributed, it is to be noted that the foregoing examples of procedure call for all of the following conditions:

- (a) Separate phases for hydrolysis of the hemi-cellulose and of the cellulose;
- (b) Separate treatment of the solutions formed in the A-stages and those formed in the B-stages;
- (c) Separate withdrawal from the system of the A-solution and the B-solution (or solutions);
- (d) Maintenance of proper temperatures in each stage;
- (e) Use of dilute solutions of SO_2 as the hydrolyzing liquid;
- (f) Circulation of the acid within the digesters;
- (g) Contact of successive batches of hydrolyzing liquid with a given digester charge; and
- (h) Countercurrent flow of the formed solutions.

I claim:

1. A commercial process for hydrolyzing substantially all of the carbohydrate content of wood to obtain a readily fermentable pentose-rich sugar liquor and at least one separate hexose-rich liquor suitable for crystallization of the glucose content thereof, said process including a plurality of first low temperature hydrolyzing steps performed at temperatures in the range above 155° C. to below 170° C. at the corresponding pressure with an aqueous pentose sugar liquor adjusted to a content of SO_2 as hydrolyzing agent in an effective amount not exceeding 2.0%, a plurality of second low temperature hydrolyzing steps performed at temperatures higher than that of said first low temperature hydrolyzing steps and in the range above 155° C. to below 170° C. at the corresponding pressure with an aqueous hydrolyzing solution containing SO_2 as hydrolyzing agent in an effective amount not exceeding 2.0%, a plurality of first high temperature hydrolyzing steps performed at temperatures in the range above 170° C. to 205° C. at the corresponding pressure with an aqueous hexose sugar liquor adjusted to a content of SO_2 , as hydrolyzing agent, in an effective amount not exceeding 2.0%, and a plurality of each of a second, a third, and so on high temperature hydrolyzing steps each of which is performed under conditions as defined for said first high temperature hydrolyzing steps, the liquid being main-

tained in lively circulation in each of said hydrolyzing steps for the duration thereof, said process comprising the steps of performing a first low temperature hydrolysis on a fresh second batch of said wood, the liquor for said hydrolysis having been drawn from a second low temperature hydrolyzing step on a first batch of said wood, withdrawing the readily fermentable pentose-rich liquor resulting from said first low temperature hydrolyzing step, subsequently performing a second low temperature hydrolyzing step on the partially spent second wood batch, withdrawing the pentose-rich liquor resulting from said second low temperature hydrolyzing step and employing said resulting liquor as the aqueous liquor in a first low temperature hydrolyzing step performed on a fresh third batch of said wood, performing a first high temperature hydrolyzing step on said second wood batch employing a hexose sugar liquor withdrawn from a third high temperature hydrolyzing step performed on said first wood batch, withdrawing from said second wood batch the hexose-rich sugar liquor resulting from said first high temperature hydrolyzing step performed on said second wood batch, said liquor being suited for crystallization of its glucose content, performing a second high temperature hydrolyzing step on said second wood batch employing as sugar liquor a liquor resulting from a fourth high temperature hydrolyzing step on said first wood batch, withdrawing from said second wood batch the hexose-rich liquor resulting from said second high temperature hydrolyzing step on said second wood batch, said resulting liquor being suited for crystallization of its glucose content, performing a third high temperature hydrolyzing step on said second wood batch employing as hydrolyzing liquor a liquor resulting from a fifth high temperature hydrolyzing step performed on said first wood batch, the original source of said liquor being a wash performed on a spent wood batch preceding in the treatment series said first wood batch, withdrawing from said second wood batch the liquor resulting from said third high temperature hydrolyzing step performed on said second wood batch and employing said withdrawn resulting liquor in a first high temperature hydrolyzing step performed on said third wood batch, and continuing the hereinabove defined pattern of operations with further high temperature hydrolyzing steps, further spent wood batch washing steps, and the corresponding number of wood batches until substantially the total amount of carbohydrate in all of said wood has been hydrolyzed.

2. A process for hydrolyzing substantially all of the cellulosic content of wood to produce a pentose-rich liquor and at least one separate hexose-rich liquor, said process including a plurality of each of the following hydrolyzing steps each of which is performed at a pressure corresponding to the temperature defined, each of which employs an aqueous hydrolyzing solution adjusted to a content of SO_2 as hydrolyzing agent in an effective amount not exceeding 2.0% and in each of which said aqueous hydrolyzing solution is maintained in lively circulation substantially for the duration of the hydrolysis: (a) low temperature hydrolysis performed at a temperature in the range from above 100°C. to below 170°C. , (b) high temperature hydrolysis performed at a temperature above 170°C. , and said process comprising performing a low temperature hydrolysis of each of a plurality of successive

batches of wood, separately withdrawing the pentose-sugar liquor resulting from each of said low temperature hydrolysis steps, performing another low temperature hydrolysis of each of said wood batches subsequent to the withdrawal therefrom of the pentose-sugar liquor resulting from the first named low temperature hydrolysis, separately withdrawing the pentose-sugar liquors resulting from each second named low temperature hydrolysis of each of said wood batches, performing a high temperature hydrolysis of each of said wood batches subsequent to the withdrawal therefrom of the pentose liquors resulting from said second named low temperature hydrolysis thereof, separately withdrawing the hexose sugar liquors resulting from each of said high temperature hydrolysis steps of said wood batches, performing another high temperature hydrolysis of each of said wood batches subsequent to the withdrawal therefrom of the hexose liquors resulting from the first named high temperature hydrolysis thereof, separately withdrawing the hexose sugar liquors resulting from the second named high temperature hydrolysis of each of the wood batches, maintaining said plurality of wood batches as a cooperative cyclic series of wood batches, passing withdrawn pentose liquor resulting from a low temperature hydrolysis of each of said wood batches in countercurrent fashion to a low temperature hydrolysis performed upon a succeeding wood batch in said cyclic series of wood batches for employment in the hydrolyzing solution thereof, passing a hexose liquor withdrawn from a high temperature hydrolysis of each of said wood batches in countercurrent fashion to a high temperature hydrolysis performed upon a succeeding wood batch in said cyclic series for employment in the hydrolyzing solutions thereof, and maintaining the pentose liquors withdrawn from said wood batches separately from the hexose liquors withdrawn therefrom.

3. A process as defined in claim 2 wherein the defined countercurrent passage of low temperature liquor comprises introducing the withdrawn pentose liquor resulting from the second named low temperature hydrolysis of each of said wood batches into the first named low temperature hydrolysis of the respectively next succeeding wood batch of said series of wood batches, the aqueous hydrolyzing solution employed in each of the second named low temperature hydrolysis steps being prepared from fresh water, and the separately withdrawn pentose sugar liquor resulting from the first low temperature hydrolysis of each of said wood batches being collected as a fermentable product.

4. A process as defined in claim 3 wherein a plurality of additional successive high temperature hydrolysis steps are performed upon each of the wood batches in said cyclic series subsequent to the withdrawal therefrom of the hexose liquor resulting from the second named high temperature hydrolysis, the hexose sugar liquor resulting from each of the additional successive high temperature hydrolysis steps being withdrawn from each of said wood batches prior to the performance of the next succeeding high temperature hydrolysis step.

5. A process as defined in claim 4 wherein the withdrawn hexose sugar liquor resulting from the first named high temperature hydrolysis of each of said wood batches is collected as a ready hexose product, at least one water wash step is performed upon the spent wood of each of said wood

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batches subsequent to withdrawal therefrom of the hexose liquor resulting from the last of the additional successive high temperature hydrolysis steps, and the wash water resulting from each of the wash steps performed on each batch of wood is passed to the wood batch next succeeding in the series of wood batches and comprises the major portion of the aqueous hydrolyzing solution for performance of one of the additional successive high temperature hydrolysis steps performed on said next succeeding batch.

6. A process as defined in claim 5 wherein each of the low temperature hydrolysis steps is performed at a temperature in the range from above 155° C. to below 170° C., and each of the high temperature hydrolysis steps is performed at a temperature in the range from above 170° C. to below 205° C.

7. A process as defined in claim 6 wherein the second named low temperature hydrolysis performed on each of said wood batches is at a temperature higher than the first named low temperature hydrolysis of said wood batch.

8. A process as defined in claim 6 wherein the pattern of operations is extended to include additional high temperature hydrolyzing steps, additional spent wood batch washing steps, and a corresponding number of wood batches until substantially the total amount of carbohydrate in all of said wood has been hydrolyzed.

9. A process as defined in claim 6 wherein the withdrawn hexose liquor resulting from the second named high temperature hydrolysis of each of said wood batches is collected as a ready hexose solution.

10. A process as defined in claim 6 wherein subsequent to introduction of the aqueous solution to each wood batch in each hydrolysis step and provision of the requisite temperature, pressure, and solution circulation conditions therein,

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pure SO₂ is introduced into the solution whereby the solution content thereof is adjusted to the defined amount.

11. A process as defined in claim 6 wherein each low temperature hydrolysis of a given batch of said wood has a duration of 1.5-4 times that of each high temperature hydrolysis of said batch.

12. A process as defined in claim 6 wherein the withdrawn hexose liquors resulting from sixth, fifth, fourth and third high temperature hydrolysis steps of each of said wood batches are passed respectively to fourth, third, second and first high temperature hydrolysis steps of the next succeeding wood batch.

13. A process as defined in claim 6 wherein the withdrawn hexose liquors resulting from sixth, fifth and fourth high temperature hydrolysis steps of each of said wood batches are passed respectively to third, second and first high temperature hydrolysis steps of the next succeeding wood batch, and withdrawn hexose liquors resulting from first, second and third high temperature hydrolysis steps of each of said wood batches are separately collected as three ready hexose solutions.

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