

# United States Patent

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**Continuation-in-part of application Ser. No.**  
**618,360, Feb. 24, 1967, now abandoned.**

[54] **PROCESS FOR PREPARING CELLULOSE PULP BY**  
**ALKALINE DIGESTION WHILE INHIBITING**  
**EXTRACTION OF HEMICELLULOSE**  
**16 Claims, 3 Drawing Figs.**

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[56] **References Cited**

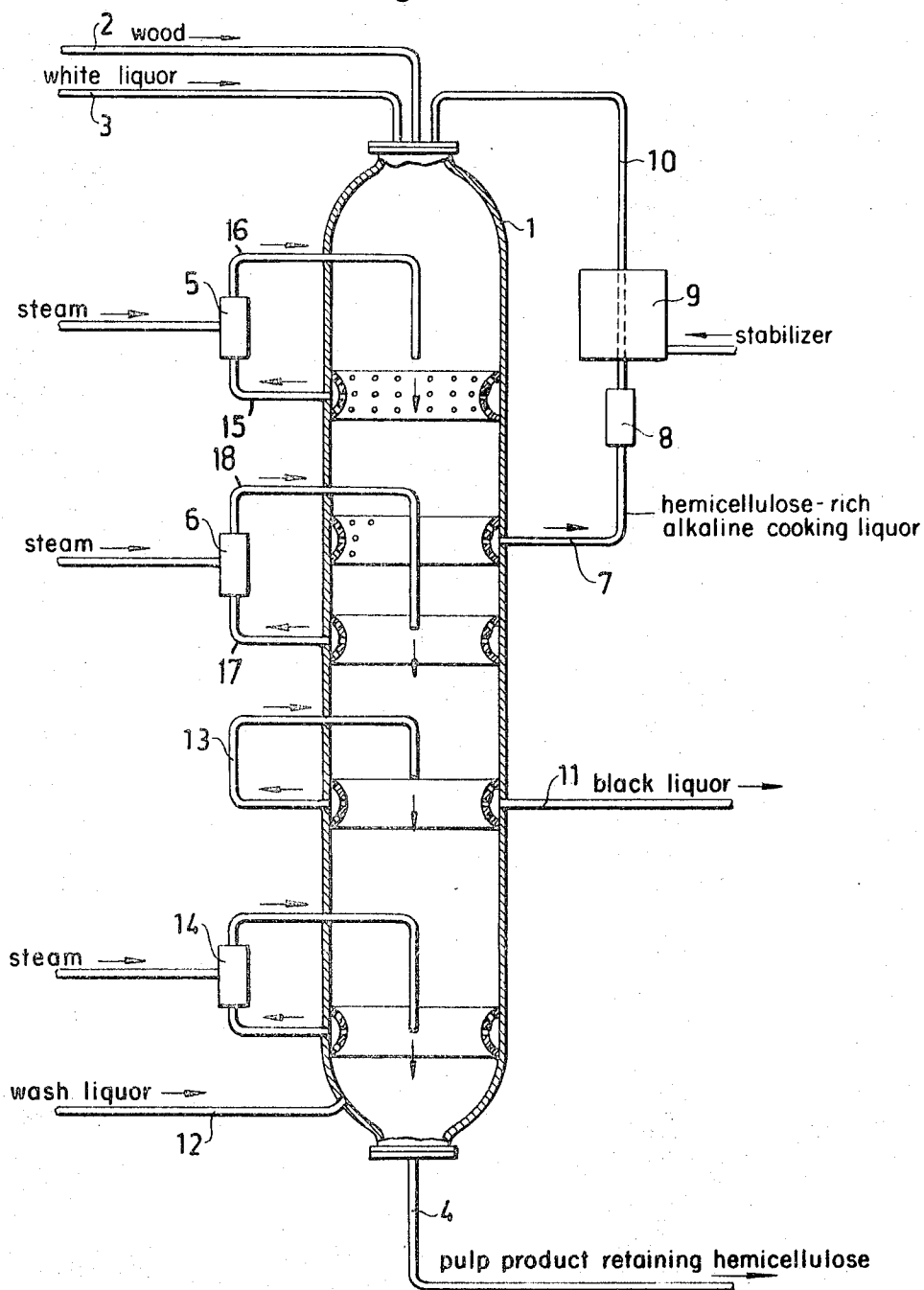
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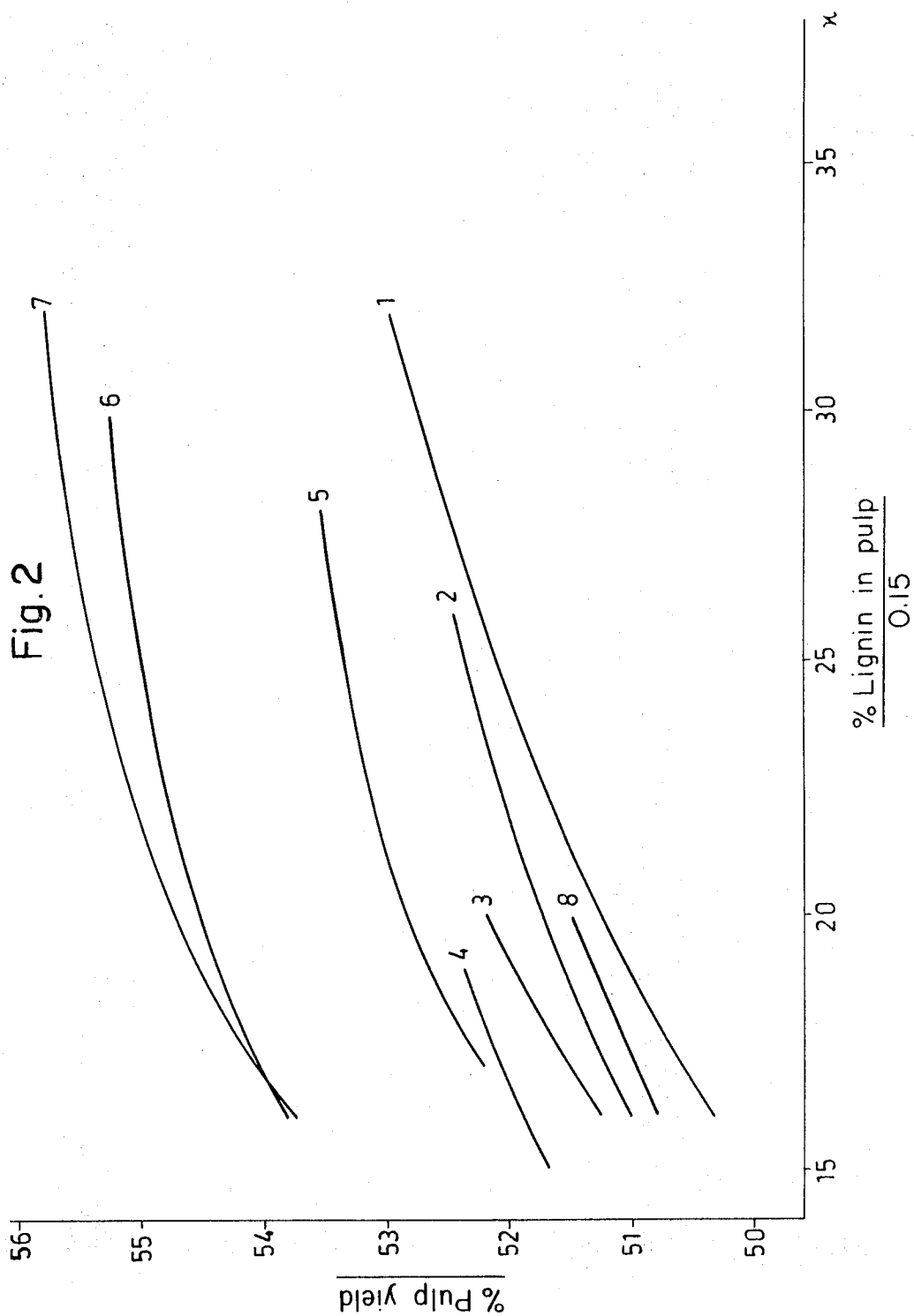
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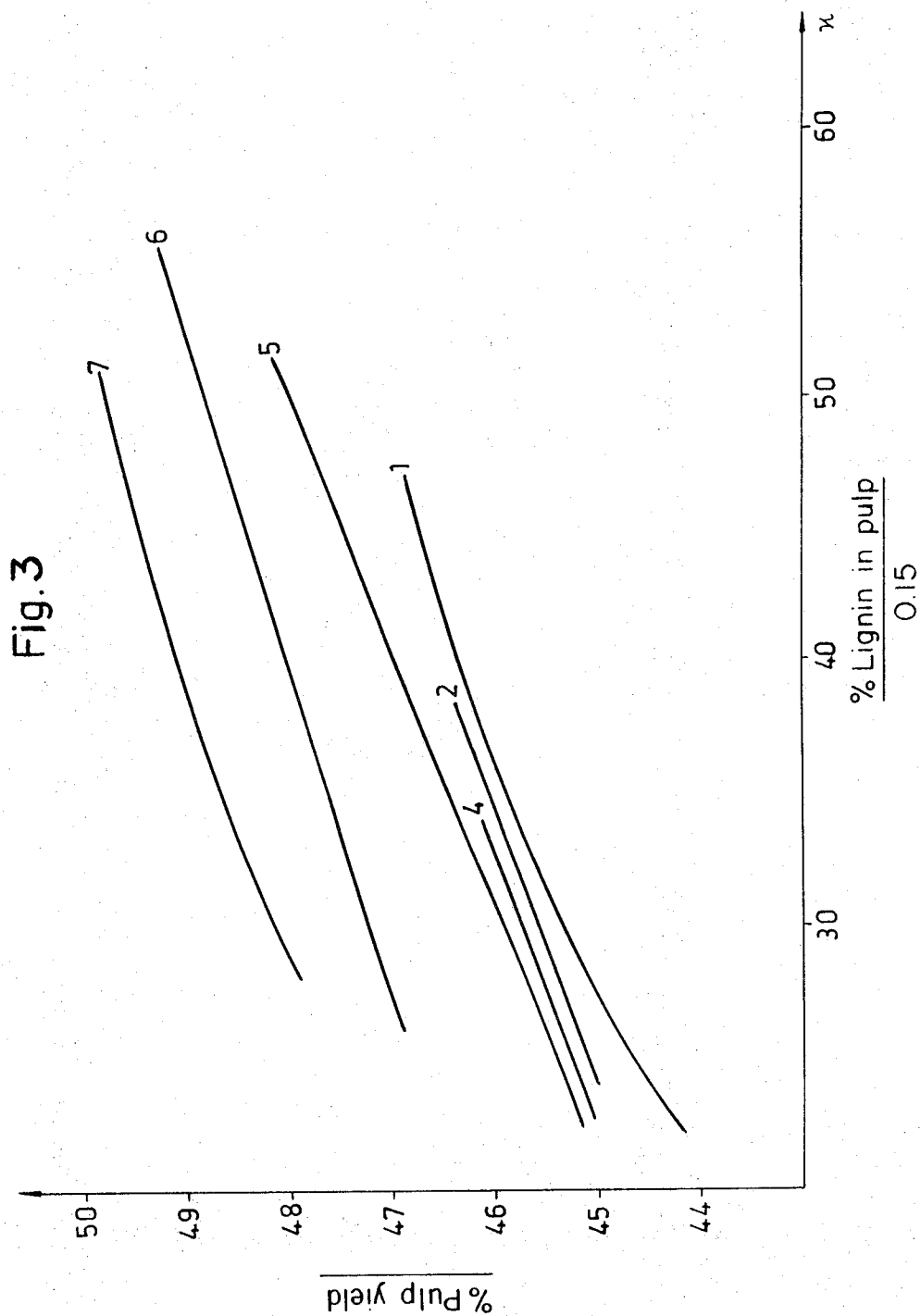
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**ABSTRACT:** A process is provided for preparing cellulose pulp by the alkaline digestion of lignocellulosic material while inhibiting extraction of hemicellulose by employing an alkaline cooking liquor having a high concentration of substantially nondegraded hemicellulose having a degree of polymerization of at least 80. The cellulose pulp product thus contains within its fibers much or substantially all of the hemicellulose present in the natural lignocellulosic material.

Fig. 1







# PROCESS FOR PREPARING CELLULOSE PULP BY ALKALINE DIGESTION WHILE INHIBITING EXTRACTION OF HEMICELLULOSE

This application is a continuation-in-part of Ser. No. 618,360, filed Feb. 24, 1967 and now abandoned.

The present invention relates to a process for the manufacture of cellulose pulp by alkaline cooking or digestion of lignocellulosic material, such as wood, while inhibiting the extraction or dissolution of hemicellulose from the lignocellulosic material during the alkaline cooking process to thereby produce a pulp containing within the pulp fibers more of the hemicellulose originally present in the lignocellulosic material than has been retained previously.

FIG. 1 is a sectional view of a digestion apparatus which can be employed in accordance with the instant invention.

FIGS. 2 and 3 plot lignin-free yield against kappa number.

The term "hemicellulose" is used in the usual sense to include all polysaccharides naturally present in lignocellulosic material which can be dissolved in aqueous solutions of alkali. Hemicellulose mainly comprises hexosans, such as glucomannans, pentosans, such as xylan, which may contain uronic acids, and nonglucose polysaccharides such as arabinogalactans, and also includes a number of cellulose degradation products. The total percentage of hemicellulose in different types of lignocellulosic material varies, and can be within the range, for example, from about 1 to about 2 percent in soft wood, and from about 22 to about 35 percent in hard wood.

In the manufacture of cellulose pulp by the alkaline digestion of a lignocellulosic material, such as wood, the wood is progressively heated or cooked in an alkaline cooking liquor at a predetermined temperature until it is delignified to the desired degree. The alkaline cooking liquor employed varies depending on the type of process employed. For example, in the kraft process, the alkaline liquor comprises a mixture of white liquor and black liquor and includes an alkaline material, such as sodium hydroxide, and neutral or alkali metal salts, such as sodium sulfate, sodium carbonate, sodium sulfide, sodium sulfite, sodium hydrosulfide and sodium thiosulfate and water. The black liquor is merely white liquor which has been employed in an alkaline digestion process and thus contains dissolved hemicellulose and other organic materials extracted from the lignocellulosic material. The cooking liquor employed in the soda process is based on a mixture of large amounts of sodium hydroxide and relatively small amounts of sodium carbonate, and includes some or all of the salts employed in the cooking liquor of the kraft process. The sodium hydroxide and the salts in the cooking liquor function to open the alkylaryl ether bonds of lignin in the lignocellulosic material, to produce lignin degradation products which are soluble in the alkaline medium. In both the kraft and soda processes, wood is normally cooked at a temperature within the range from about 50° to about 190° C. for varying periods of time, depending upon the type of wood being cooked, and the properties desired in the pulp product.

Lignocellulosic material contains relatively large quantities of hemicellulose. During the alkaline cooking of the lignocellulosic material, a large portion of the hemicellulose, up to 10 percent, based on the dry wood weight, is extracted into the cooking liquor, and an additional 10 to 15 percent may be extracted and degraded. The percentage of hemicellulose extracted from the lignocellulosic material and dissolved in the cooking liquor increases to a maximum during the first portion of the cooking process, while the temperature is being raised to the maximum level, and then falls, due to degradation of the hemicellulose into soluble products. However, very little, if any, of the hemicellulose is precipitated onto the cellulose, and thus a substantial amount of the hemicellulose is lost.

The presence of hemicellulose in cellulose pulp is often desired. High hemicellulose paper pulp increases in strength more quickly on beating than does pulp containing little or no hemicellulose. Furthermore, paper manufactured from high-hemicellulose pulp generally has a greater breaking length (tensile strength), although it may have a somewhat reduced tearing strength. Thus, in many instances, it would be desira-

ble to inhibit the dissolution of hemicellulose from the lignocellulosic material being cooked in alkaline cooking liquor, so as to ensure that as much as possible of the hemicellulose naturally present in the wood remains in the cooked pulp.

To restore hemicellulose lost by extraction, attempts have been made to combine with the cellulose pulp the hemicellulose extracted from previously cooked lignocellulosic material, and dissolved in the cooking liquor. For example, a cooking liquor high in hemicellulose has been removed during the cook, and returned to the cooking liquor at the final stage of the cook, in order to precipitate hemicellulose onto the pulp fibers. However, this procedure has not been too successful, because active alkali is also withdrawn from the cooking process with the hemicellulose, and returned to the final stage of the cooking process and thus inhibits the precipitation of the hemicellulose. In order to promote precipitation of the hemicellulose from the cooking liquor onto the pulp fibers, acid has been added to the cooking liquor rich in hemicellulose. However, this results in an undesirable consumption of acid and alkali, which could otherwise have been used in the digestion process. In both cases, hemicellulose precipitated onto the fibers of the pulp product is not returned to within the fibers in the condition in which it was originally present in the lignocellulosic material, but lies on the surface. Here, it is easily lost in subsequent processing. Thus, for example, when the pulp is submitted to bleaching operations, much of the hemicellulose precipitated on the pulp fibers is removed.

In normal sulfate pulping, a portion of black liquor (liquor drawn off at the end of the cooking process) is recycled for use in the next cooking process. The purpose of this step is to increase the solids content of the cooking liquor containing the substantially cooked wood. The recycled black liquor contains of course, a certain amount of hemicellulose. However, the hemicellulose dissolved in the black liquor is substantially degraded during the latter portion of the cooking period, i.e. the time during which the cook is held at maximum temperature (normally 150° to 190° C.) and has no appreciable influence on the percentage of hemicellulose in the pulp produced in the next cooking.

U.S. Pat. No. 1,737,590 to Johnsen describes a cooking process using an acid or neutral cooking liquor to which soluble carbohydrates are added, such as hexoses, pentoses and hexosans and pentosans. These are the hydrolysis products of the carbohydrates present in the wood, and can be added as waste cooking liquor from a previous cooking operation. However, the hydrolyzed or degraded carbohydrates are not effective in inhibiting solution of the nonhydrolyzed hemicellulose of the wood. Moreover, Johnsen removes the lignin content from the cooking liquor before recycling it.

The present invention provides a process for preparing cellulose pulp by the alkaline digestion of lignocellulosic material, retaining in the pulp as much as possible of the hemicellulose originally present in the lignocellulosic material. Whereas in the normal process, a hemicellulose retention of 40 percent or even lower is normal, in the process of the invention, hemicellulose retention of about 50 percent or more is obtainable. The hemicellulose that is retained is not extracted at all, and so it remains in its original condition in the fibers, and thus an increase in yield of pulp is obtained and hemicellulose in the pulp is not lost during subsequent treatment of the pulp, e.g., on bleaching.

In accordance with the invention, the hemicellulose originally present in the lignocellulosic material to be cooked is substantially prevented from being extracted from the lignocellulosic material and from being dissolved in the alkaline cooking liquor during the cook, by providing a high concentration of substantially nondegraded hemicellulose in the alkaline cooking liquor at the beginning of the digestion. Preferably, the alkaline cooking liquor has as high a concentration as possible of substantially nondegraded hemicellulose, and preferably at least 1 percent by weight of the cooking liquor.

Thus, in accordance with the process of the instant invention for preparing cellulose pulp by alkaline digestion of lignocellulosic material, lignocellulosic material is heated in an alkaline cooking liquor containing dissolved substantially nondegraded hemicellulose, at a digestion temperature below that at which dissolved hemicellulose is degraded or decomposed and for a time to convert the lignocellulosic material to pulp. After cooking, the alkaline liquor can be withdrawn and the alkali concentration restored, after which the alkaline liquor can be used for a further cooking operation, due to the fact that the dissolved hemicellulose is not materially degraded or decomposed.

The degree of degradation or decomposition of hemicellulose is measured, in accordance with the invention, in terms of the degree of polymerization of the hemicellulose. If the degree of polymerization is low, the degree of degradation is high. A hemicellulose that is substantially not degraded nor decomposed, in accordance with the invention, has a degree of polymerization, abbreviated  $\overline{DP}_n$ , of at least 80, preferably at least 100, and most preferably at least 120.

The determination of  $\overline{DP}_n$  is according to the procedure described at page 697 of the article by S. Axelsson et al., "Dis-solution of Hemicellulose During Sulfate Pulping," Svensk Papperstidning 1962 693 No. 18 (Sept. 30, 1962). This procedure is as follows:

The cooking liquor (400 ml.) is neutralized with acetic acid and poured into alcohol (1600 ml.). The precipitate is isolated by centrifugation, washed three times with alcohol: water (40:1), three times with alcohol, three times with ether and dried in vacuo.

The fraction (2 g.) is delignified with 10 ml. chlorine dioxide solution (20 g.  $\text{ClO}_2/\text{l}$ ) and the hemicellulose recovered by precipitation with alcohol. The  $[\eta]$  is determined viscometrically, using a Wagner-Russel viscosimeter. Cupriethylene solution (0.25 M) is used as solvent. The dilution to different concentrations is made in the viscosimeter. The  $\overline{DP}_n$  is calculated from  $\overline{DP}_n = K \cdot [\eta]$ . The constant is given the value 212 according to Glaudemans, and Timell, Svensk Papperstidning 61 (1958) 1.

An alkaline cooking liquor having a high concentration of substantially nondegraded hemicellulose can be prepared by heating an alkaline cooking liquor and a lignocellulosic material to the maximum temperature at which the cook is to be carried out. This temperature is within the range from about 25° C. to about 190° C., preferably 120° to 150° C. At this temperature, it is assured that the concentration of hemicellulose extracted from the lignocellulosic material in the alkaline cooking liquor will be at a maximum, and this will inhibit further dissolution from the lignocellulosic material to be treated therewith. Such an alkaline cooking liquor usually has a concentration of at least 1 percent up to about 10 percent hemicellulose. The liquor is withdrawn when ready, cooled, and mixed with lignocellulosic material for the cook in accordance with the invention. The liquor can be reused for a number of cooks, if the alkali concentration is replenished.

The instant process can in this way be carried out continuously by using a long-dwell digester tower, and recirculating the alkaline cooking liquor. The alkaline cooking liquor having a high concentration of hemicellulose is withdrawn from the digester at a temperature below that at which hemicellulose is degraded, within the range from about 100° C. to about 170° C., according to the process used, cooled preferably to below 120° C., recycled to the beginning of the digester for blending with fresh lignocellulosic material, and the alkali concentration replenished by addition of the necessary amount of fresh cooking liquor, i.e. white liquor. The withdrawal of the cooling liquor is performed in such a manner and in such an amount that the amount of alkali retained in the pulp is sufficient to complete the delignification of the pulp.

The yield obtained in the process of the instant invention can be advantageously improved by admixing in the alkaline cooking liquor a compound capable of improving the re-

sistance of the hemicellulose in the lignocellulosic material and in the cooking liquor to degradation at the cooking temperatures. The stabilizer is added to the hemicellulose containing liquor in an amount within the range from about 0.1 to about 3 percent by weight of the lignocellulosic material. Examples of stabilizers which inhibit degradation of hemicellulose and which are suitable for use herein include alkali metal and ammonium polysulfides, such as sodium polysulfide, potassium polysulfide, lithium polysulfide and caesium polysulfide; alkali metal borohydrides, such as sodium borohydride, potassium borohydride, lithium borohydride, rubidium borohydride, and caesium borohydride; hydrazine, and hydrazine derivatives. Sodium polysulfides are the preferred stabilizers.

Degradation of the hemicellulose can also be inhibited by keeping the temperature of the hemicellulose-containing alkaline cooking liquor below about 120° C. as much as possible.

The process of the instant invention is applicable to all types of alkaline cellulose pulping processes, including the sulfate and soda processes, as batchwise and continuous operations.

In the case of both batch and continuous alkaline cooking processes, the ratio of alkaline cooking liquor: lignocellulosic material is within the range from about 3:1 to about 4.5:1. The mixture of liquor and lignocellulosic material is progressively heated from the starting temperature of from 50° to 100° C. to the maximum cooking temperature, within the range of from about 150° to about 190° C., over a cooking time within the range of from about three-fourths to about 4 hours. The maximum temperature is maintained for a time within the range of from about one-half to about 5 hours.

As the concentration of hemicellulose that can be reached in an alkaline cooking liquor is a function of alkali concentration, digestion temperature and time, the concentration of hemicellulose at the start should be as close as possible to that reached in a digestion under identical or comparable temperatures and times. Of course, since the recycled liquor is usually diluted with water and white liquor, it is not quite possible to reach this concentration. Usually, the amount of hemicellulose present in the liquor is within the range from about 1 percent to about 10 percent by weight of the liquor. The alkaline cooking liquor should preferably be removed from the lignocellulosic material when the maximum digestion temperature has been reached, or before this. Care should be taken so that the liquor is drawn off before a temperature is reached at which the hemicellulose is degraded to an undesirable degree.

The digestion temperature and time and alkali concentration depend on the kind of wood pulped. For example, where pine wood is to be cooked, the cooking liquor is drawn off at a temperature of at least 120° C. and suitably within the range from about 130° to about 170° C. and preferably from about 160° to about 170° C., and in the case of birch at a temperature of at least 120° C. and suitably within the range of from about 130° to about 170° C., and preferably from about 150° to about 160° C. As much liquor as possible should be drawn off so as to maintain the supply of recirculating cooking liquor, and prevent contamination of the pulp with cooking liquor degradation products during the remainder of the digestion, which takes place at maximum temperature. There must be a sufficient amount of alkali remaining to complete the delignification. This as a rule means that enough liquor should be withdrawn so that the ratio of liquor remaining to wood to be digested is within the range from about 1:1 to about 2.5:1 and preferably about 2:1. The digestion is then terminated in vapor phase, by cooking at or about the maximum temperature for from one-half to about 5 hours. The withdrawn liquid is cooled, and supplied with a stabilizer, if desired.

The alkaline cooking liquor should have an amount of alkali within the range from about 10 to about 35 percent, preferably 15 to 25 percent by weight of the lignocellulosic material.

FIG. 1 is a sectional view of a digestion apparatus which can be employed in carrying out a continuous alkaline cooking process in accordance with the instant invention. The apparatus comprises an elongated digester vessel 1 containing conduits or inlets 2 and 4 for wood and white liquor, respectively, and outlet 4 for the cellulose pulp product. Steam heaters 5 and 6 are provided for heating liquor circulating from the digester vessel 1 via pipes 15 and 16, 17 and 18, respectively. The digester 1 is equipped with an alkaline liquor recycle line, composed of withdrawal line 7, cooler 8, mixer 9, and recycle feed conduit 10 for recycling the hemicellulose-containing cooking liquor. Digester 1 is also provided with outlet 11 for withdrawal of the residual cooking liquor (black liquor) after cooking is completed, separation recirculation conduit 13 and wash liquor introduction conduit 12 for washing the pulp prior to discharging it from the digester 1 via line 4, and heater 14 for heating the wash liquor.

In carrying out the process of the instant invention employing the apparatus of FIG. 1, a lignocellulosic material, e.g. wood, alkaline cooking liquor containing a high concentration of substantially nondegraded hemicellulose (recycled via lines 7 and 10) and white liquor for alkali replenishment of the alkaline liquor, are introduced through conduits 2, 10 and 3, respectively, into the top of the elongated digester 1. As the mixture travels downwardly through the digester to line 7, the mixture is gradually brought to a temperature of from 110° to 160° C. by circulation through heater 5. The alkaline cooking liquor is drawn off through the conduit 7, cooled to 50° to 120° C. in cooler 8, mixed with polysulfide stabilizer in mixer 9, and recycled to the top of the digester 1 via conduit 10. The remaining liquor and wood contents of the digester are gradually brought to a temperature of from 150° to 190° C., as they progress downwardly from line 7, by circulating through heater 6, to complete the cooking, and move downwardly through the digester to line 11. Black liquor is removed through the conduit 11, which is at the completion of the digestion. The digested pulp is countercurrently washed with washing liquor introduced through conduit 12, recirculated and heated in heater 14 via lines 20 and 21. The washed pulp is finally removed from the digester via line 4.

The rates of withdrawal of alkaline recycled liquor, black liquor, and wood pulp and the rate of introduction of wash liquor are adjusted according to the digestion conditions desired, and will vary with the type of wood and digestion time and temperature, and the alkali concentrations.

The lignocellulosic material which can be converted to cellulose pulp in accordance with the instant invention includes wood, in any form such as wood chips, shavings, sawdust, splinters, etc. and includes wood containing alkylaryl ether lignin bonds, such as spruce, pine, redwood, larch, Douglas fir, hemlock, and wood from deciduous trees such as birch, oak, aspen, beech, eucalyptus, and other lignocellulosic materials such as straw, bagasse, bamboo, and rushes.

The process of the instant invention gives an increased pulp yield over that obtained in conventional alkaline digestion processes. For example, when pine wood is employed as the lignocellulosic material, the invention provides an increase in yield of pulp product of approximately 0.3 percent (calculated on the weight of wood cooked) without using a stabilizer, and an increase in yield of up to about 3.5 percent when a stabilizer is used. When birch wood is cooked, the instant process provided an increase in yield of pulp product of about 0.6 percent without a stabilizer and 3.5 percent with a stabilizer. In the case of a pulp plant manufacturing 100,000 tons of pulp each year, an increase in yield of 1 percent (based on the weight of wood cooked) means approximately 2,000 tons of pulp for birchwood and approximately 2,200 tons of pulp for pinewood.

The following examples in the opinion of the inventors represent preferred embodiments of their invention.

## EXAMPLE 1

Air-dry birch chips, free of visible knots and bark, were submitted to alkaline digestion in accordance with the process of the instant invention (Runs 5 to 7) and in accordance with prior art processes (Runs 3, 4 and 8) and with other comparable processes (Runs 1 and 2). The digester employed in all runs was a 2-liter autoclave in an electrically heated glycol bath. The charge of birch chips and alkaline cooking liquor (having the composition set out below), was introduced into the digester and heated up. When a temperature of 150° C. had been reached in the digester, an amount of alkaline cooking liquor corresponding to somewhat more than half the amount of alkaline liquor in the digester was drawn off. The withdrawn liquor was cooled, and analyzed with respect to active alkali and sulfide. Certain portions were stabilized with a polysulfide in the following manner: an amount of liquor which corresponded to about half the liquor: wood ratio at the beginning of the digestion process was heated to 100° C., admixed with polysulfide and then allowed to stand at 100° C. for 15 min.

The recycled liquor (stabilized or unstabilized) containing hemicellulose was mixed with white liquor and birch chips in the digester, and the proportions of white and recycled liquors were adjusted so as to give substantially the same percentage of alkali in the cooking liquor in each cycle. Liquor was continuously drawn off from this cook in a similar manner at 150° C., stabilized in the same way as the liquor previously drawn off, and then returned to the digester with more birch wood and white liquor. A total of seven cooks were run using recycled alkaline cooking liquor and fresh white liquor in this way, employing the following process conditions:

|                                                               |                                                                                                                                |
|---------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|
| Process Conditions:                                           |                                                                                                                                |
| Wood-to-liquor ratio at the beginning of the cooking process. | 0.25 kg. calculated on bone dry birch wood per liter of liquor.                                                                |
| Initial cooking temperatures.                                 | Start—80° C. Maximum—105 minutes to heat up to 150° C. 150° C. for 15 minutes.                                                 |
| Liquor drawn off to a wood-to-liquor ratio of 1:2.            |                                                                                                                                |
| Final cook temperature.                                       | 150–158° C. for 15 minutes; 158° C. for 120 minutes.                                                                           |
| Chemical charges:                                             |                                                                                                                                |
| Sulfidity, Na <sub>2</sub> S/NaOH+Na <sub>2</sub> S           | 30%.                                                                                                                           |
| Alkali charge.                                                | 17 and 20% effective alkali (NaOH+½Na <sub>2</sub> S calculated at NaOH), including the alkali in the returned cooking liquor. |
| Sodium polysulfide for stabilizing hemicellulose.             | 0%, 1% and 2% sodium polysulfide-sulfur calculated on the wood.                                                                |

Upon completion of the digestion, the autoclaves containing digested pulp and residual liquor were cooled. Boiling water was added, the pulp defibrated for 2.5 minutes in laboratory defibrators, centrifugally washed, defibrated for 2.5 minutes in laboratory defibrators, and screened.

The pulps obtained were bleached in a conventional manner in six stages with chlorine, NaOH, NaOCl, ClO<sub>2</sub>, NaOH and ClO<sub>2</sub> according to the conditions appearing below:

| Bleaching conditions                        | Bleaching       |      |       |                  |      |                  |
|---------------------------------------------|-----------------|------|-------|------------------|------|------------------|
|                                             | Cl <sub>2</sub> | NaOH | NaOCl | ClO <sub>2</sub> | NaOH | ClO <sub>2</sub> |
| Pulp concentrations, percent.               | 3.5             | 8    | 8     | 6                | 8    | 6                |
| Time in hours.                              | 1               | 2    | 2     | 3                | 2    | 5                |
| Temperature, ° C.                           | 20              | 50   | 40    | 70               | 50   | 85               |
| Change of active chlorine, percent of pulp. | 10.22           | 2    | 0.9   | 0.8              | 0.7  | 1.0              |

<sup>1</sup> Multiplied by Kappa number.

The following procedures were used in Runs 5, 6 and 7, in accordance with the invention:

Run 5

The alkaline cooking liquor containing hemicellulose was withdrawn at 150° C., and recycled with white liquor.  
(Curve 5, FIG. 2)

**Run 6**

The same as Run 5, but 1 percent sodium polysulfide was added before recycling the cooking liquor.  
(Curve 6, FIG. 2)

**Run 7**

The same as Run 6, but 2 percent sodium polysulfide was added.

In addition to the above, the following runs using cooking processes were carried out for comparison with the above cooking process of the invention.

**Run 1**

At the beginning of the cooking process, fresh white liquor and water was added, but no hemicellulose-containing liquor. Half the liquor present was drawn off at 150° C.  
(Curve 1, FIG. 2)

**Run 2**

At the beginning of the cooking process fresh white liquor and black liquor were added, as is normally done when digesting sulfate pulp on a factory scale. Half the liquor present was drawn off at 150° C.  
(Curve 2, FIG. 2)

**Run 3**

Cooking as in Run 1 without drawing off liquor at 150° C.  
(Curve 3, FIG. 2)

**Run 4**

Cooking as in Run 2, but no liquor was drawn off at 150° C.  
(Curve 4, FIG. 2)

**Run 8**

Cooking as in Run 2, including drawing off liquor rich in hemicellulose at 150° C. but returning this liquor to the final stage of the digestion. (sorption digestion).  
(Curve 8, FIG. 2)

Average values of the yields in the runs according to the invention (Runs 5, 6 and 7) as compared with the other methods (Runs 1, 2, 3, 4, and 8) are shown in the following table. Lignin-free yield refers to the percent pulp product based on weight of lignocellulosic material cooked.

TABLE I

| Run No. | Method                                                         | Total<br>mean<br>lignin-free<br>yield | Mean<br>Kappa-<br>number | Active alkali, percent of wood |                  |
|---------|----------------------------------------------------------------|---------------------------------------|--------------------------|--------------------------------|------------------|
|         |                                                                |                                       |                          | Charged                        | Charged+recycled |
| 1.....  | Withdrawal of liquor, water added, no recycling.....           | 52.4                                  | 2                        | 20.0                           | -----            |
| 2.....  | Withdrawal of liquor, black liquor added, no recycling.....    | 50.65                                 | 1.3                      | 23.6                           | -----            |
| 3.....  | No withdrawal of liquor, water added, no recycling.....        | 52.4                                  | 2.3                      | 19.8                           | 20.2             |
| 4.....  | No withdrawal of liquor, black liquor added, no recycling..... | 50.8                                  | 1.0                      | 23.3                           | 23.7             |
| 5.....  | Withdrawal, recycling liquor (0% polysulfide).....             | 52.2                                  | 2.0                      | 20.0                           | -----            |
| 6.....  | Withdrawal, recycling liquor (1% polysulfide).....             | 51.2                                  | 1.0                      | 23.6                           | -----            |
| 7.....  | Withdrawal, recycling liquor (2% polysulfide).....             | 52.1                                  | 17.5                     | 19.8                           | 20.2             |
| 8.....  | Sorption digestion.....                                        | 51.75                                 | 15.3                     | 23.3                           | 23.7             |
|         |                                                                | 53.4                                  | 25.0                     | 17.4                           | 20.9             |
|         |                                                                | 52.5                                  | 18.1                     | 19.5                           | 24.4             |
|         |                                                                | 55.1                                  | 26.0                     | 18.0                           | 22.1             |
|         |                                                                | 54.0                                  | 16.9                     | 20.1                           | 25.3             |
|         |                                                                | 55.6                                  | 28.9                     | 18.6                           | 22.8             |
|         |                                                                | 54.3                                  | 18.0                     | 20.6                           | 26.2             |
|         |                                                                | 51.3                                  | 19.0                     | 23.6                           | 23.6             |
|         |                                                                | 50.8                                  | 16.9                     | 23.6                           | 23.6             |

<sup>1</sup> In the case of cooking where polysulfide was added at the beginning of the process; requires an extra alkali charge of 0.4% per charged percent polysulfide sulfur (on low sulfidities). If the sulfidity is high, a higher alkali charge is necessary.

<sup>2</sup> With H<sub>2</sub>SO<sub>4</sub> additive in the final stage of the cooking process.

As can be seen from table I, the cooking processes carried out according to the invention i.e., Runs Nos. 5, 6 and 7, have a considerably increased yield as compared with remaining cooks.

In table II below are shown the bleaching yields for these cooking runs. The bleach yield drops with high kappa numbers, owing to the fact that the pulp then contains more lignin, which is bleached away. The bleaching yields are highest for cooking processes in which liquor is returned according to the invention (Runs Nos. 5, 6 and 7) which shows that the thus-produced pulp withstands bleaching equally as well as conventionally digested pulp.

TABLE II

| Run No. | Method                                                          | Kappa-number | Bleaching yield |
|---------|-----------------------------------------------------------------|--------------|-----------------|
| 1.....  | Withdrawal of liquor, water added.....                          | 24.9         | 93.7            |
| 2.....  | Withdrawal of liquor, black liquor added.....                   | 17.9         | 96.2            |
| 3.....  | No withdrawal of liquor, water added.....                       | 25.0         | 92.5            |
| 4.....  | No withdrawal of liquor, black liquor added.....                | 15.5         | 95.7            |
| 5.....  | Withdrawal of liquor, recycling liquor 0% polysulfide.....      | 20.0         | 95.0            |
| 6.....  | Withdrawal of liquor, recycling liquor 1% polysulfide.....      | 15.8         | 95.5            |
| 7.....  | Withdrawal of liquor, recycling liquor 2% polysulfide.....      | 17.5         | 95.0            |
| 8.....  | Sorption digestion:                                             | 15.3         | 96.3            |
|         | Withdrawal of liquor, H <sub>2</sub> SO <sub>4</sub> added..... | 25.1         | 93.5            |
|         | Withdrawal of liquor, no H <sub>2</sub> SO <sub>4</sub> .....   | 17.3         | 97.4            |
|         | No withdrawal, H <sub>2</sub> SO <sub>4</sub> added.....        | 25.1         | 94.4            |
|         |                                                                 | 16.6         | 96.4            |
|         |                                                                 | 29.0         | 92.1            |
|         |                                                                 | 16.3         | 96.1            |
|         |                                                                 | 17.8         | 95.5            |
|         |                                                                 | 16.8         | 95.3            |
|         |                                                                 | 18.7         | 94.9            |

The lignin-free yield of pulp obtained for the eight runs made is plotted in FIG. 2 against kappa number (which can be converted into the percent lignin present in the pulp product by multiplying by 0.15). The comparison between the various cooking methods was made at kappa no. 18. This kappa number is considered normal in factory cooking of birch.

Curve 1 shows that Run 1 using fresh white liquor as the cooking liquor, gave the lowest yield. Hemicellulose was dissolved in the liquor during cooking, and was drawn from the charge; the yield is thus low.

A cook like Run 1 where no liquor is drawn off, so a minimum of hemicellulose is lost in the liquor, is represented by Curve 3. The yield in this case lies approximately 0.9 percent higher than in curve 1.

Curves 2 and 4 show the yield in the case when black liquor containing degraded hemicellulose, removed from the final stage of the cooking process, was used instead of fresh water in preparing the cooking liquor, with withdrawal of liquor (Run 2) and without withdrawal (Run 4).

Substantially higher yields were obtained when in accordance with the process of the instant invention, Runs 5 to 7, an alkaline liquor high in hemicellulose was withdrawn from the digester, replenished with white liquor, and recycled to the start of the digestion. Run 5 (Curve 5) have a yield a little more than 0.6 percent above Run 3. When the recycled liquor (Curves 6 and 7) was stabilized with polysulfide, a 2.5 percent higher yield was obtained than in Run 3. A normal polysulfide cook gives approximately 1 percent yield-gain per added percent polysulfide sulfur.

It can be seen from Curve 8 that the increase in yield was very small when withdrawn liquor rich in hemicellulose was

returned to the final stage of the cooking process and in fact even lower than in the case of a conventional cook where no liquor was drawn off (Runs 3 and 4).

The degree of polymerization ( $\overline{DP}_n$ ) of the hemicellulose recycled in Runs 5 to 7 was determined and found to be as follows:

| Run No. | $\overline{DP}_n$ |
|---------|-------------------|
| 5       | 149               |
| 6       | 151               |
| 7       | 152               |

This shows that the hemicellulose was not degraded to any significant degree.

### EXAMPLE 2

The procedure of Runs 1, 2, 4, 5, 6 and 7, and example 1 was repeated except that pinewood was employed instead of birchwood. The cook was heated to the temperatures set out below, liquor being drawn off at 170° C. The pulps were not bleached.

Recycling cooking liquor  
rich in hemicellulose

|                          |                                                                                                                      |
|--------------------------|----------------------------------------------------------------------------------------------------------------------|
| Wood-to-liquid ratio     | 1:4                                                                                                                  |
| Initial Cook Temperature | Start—80° C. after<br>10 min.<br>Maximum—180 min. to<br>heat up to 170° C. with<br>drawal of liquor after<br>10 min. |
| Final Cook Temperature   | 170° C. for 120 min.                                                                                                 |

In all except Run 4, half the amount of liquor was drawn off at 170° C., and returned to the first stage of the next cooking process.

Certain of the drawn off liquors were stabilized with polysulfide. Runs 1, 2 and 4 as in example 1 were effected as a comparison, with withdrawal of liquor at 170° C.

In the case of kappa number 32, the yields were as follows:

TABLE III

| Run No. | Method                                      | Total lignin-free yield* |
|---------|---------------------------------------------|--------------------------|
| 1       | withdrawal of liquor, water added           | 45.6                     |
| 2       | withdrawal of liquor, black liquor added    | 45.8                     |
| 4       | no withdrawal of liquor, black liquor added | 45.9                     |
| 5       | withdrawal of liquor, recycling of liquor   | 46.2                     |
| 6       | 0% polysulfide                              | 47.4                     |
| 7       | 1% polysulfide                              | 47.4                     |
|         | 2% polysulfide                              | 48.4                     |

\*Kappa number 32

Lignin-free yield in these runs is plotted against kappa number in FIG. 3. The difference in yield between a recycle cook without polysulfide (Run 5, Curve 5) and a cook without recirculation of the liquor (Run 1, Curve 1) was only approximately 0.5 percent, owing to the fact that the amount of hemicellulose dissolved in the liquor was not as great as in the case of birch. As can be seen from FIG. 3, the yield when cooking according to the invention (Curves 5, 6 and 7) was considerably higher than in the case of other cooking processes (Runs 2,4) used as a comparison. Stabilization with 1 percent sodium polysulfide (Run 6, Curve 6) gave a 1.5 per-

cent yield gain as compared with Curve 4, (without drawing off liquor). A further addition of 1 percent sodium polysulfide (Run 7, Curve 7) merely gave a 1 percent gain, a gain which is not more than that obtained in a normal polysulfide cooking process.

The degree of polymerization of the hemicellulose recycled in Runs 5 to 7 was determined, and found to be as follows:

| Run | $\overline{DP}_n$ |
|-----|-------------------|
| 5   | 103               |
| 6   | 104               |
| 7   | 105               |

This shows that the hemicellulose was not substantially degraded.

### EXAMPLE 3

Birch was cooked as in example 1. However, the cooking liquor was heated to 158° C. which took about 120 minutes, maintained at 158° C. for 15 minutes and then drawn off at 158° C. Only cooking processes which involved drawing off liquor and restoring said cooking liquor (with and without stabilization) were carried out (Runs 1, 3, 5, 6, 7).

Mean values for the yields in various cooking methods are given in table IV below.

TABLE IV

| Run No. | Method                     | Total lignin-free yield | Kappa number |
|---------|----------------------------|-------------------------|--------------|
| 1       | Withdrawal, water added    | 52.2                    | 25.0         |
| 3       | No withdrawal, water added | 50.4                    | 16.0         |
| 5       | Withdrawal, recycling      | 52.2                    | 20.0         |
| 6       | 0% polysulfide             | 51.2                    | 16.0         |
| 7       | 1% polysulfide             | 53.2                    | 24.5         |
|         | 2% polysulfide             | 52.2                    | 16.5         |
|         | Withdrawal, recycling      | 54.7                    | 24.0         |
|         | 1% polysulfide             | 53.8                    | 17.5         |
|         | 2% polysulfide             | 54.2                    | 27.0         |
|         |                            |                         | 18.0         |

As can be seen from the table, the cooking processes carried out according to the invention (Runs 5, 6 and 7) increased the yield as compared with Runs 1 and 3.

The degree of polymerization of the hemicellulose recycled in Runs 5 to 7 was determined and found to be as follows:

| Run No. | $\overline{DP}_n$ |
|---------|-------------------|
| 5       | 129               |
| 6       | 130               |
| 7       | 130               |

This shows the hemicellulose was not substantially degraded.

Having regard to the foregoing disclosure, the following is claimed as the inventive and patentable embodiments thereof:

1. A process for digesting lignocellulosic materials while retaining hemicellulose within the resulting cellulose pulp material, which comprises heating a lignocellulosic material in an alkaline cooking liquor containing dissolved substantially nondegraded hemicellulose in a concentration of at least 1 percent and having a degree of polymerization of at least 80 at a digestion temperature below that at which dissolved hemicellulose is degraded and for a time to convert the lignocellulosic material to pulp, and recovering a pulp product retaining a substantial proportion of the hemicellulose therewithin.

2. A process as in claim 1 wherein the alkaline cooking liquor contains at least about 2 percent by weight of substantially nondegraded hemicellulose.

3. A process as in claim 1 wherein the alkaline cooking liquor containing dissolved hemicellulose is prepared by heating an alkaline cooking liquor and a lignocellulosic material to a digestion temperature within the range from about 100 to

about 190° C. to extract hemicellulose from the lignocellulosic material and dissolve the hemicellulose in the alkaline cooking liquor.

4. A process as in claim 3, wherein the alkaline cooking liquor is cooled to a temperature below about 120° C. before it is employed in cooking lignocellulosic material.

5. A process as in claim 3 wherein a stabilizer which inhibits degradation to hemicellulose to a degree of polymerization below 80 is admixed with the alkaline cooking liquor containing dissolved hemicellulose prior to employing the cooking liquor to cook lignocellulosic material.

6. A process as in claim 5 wherein the stabilizer is added to the cooking liquor at a temperature below about 120° C.

7. A process as in claim 5 wherein the stabilizer is selected from the group consisting of alkali metal and ammonium polysulfides, alkali metal borohydrides and hydrazine.

8. A process as in claim 5 wherein from about 0.1 to about 3 percent stabilizer based on weight of lignocellulosic material is added to the alkaline cooking liquor.

9. A process as in claim 1 wherein the alkaline cooking liquor containing dissolved substantially nondegraded hemicellulose is recycled from a previous lignocellulosic material digestion carried out under conditions to maintain a degree of polymerization of the dissolved hemicellulose of at least 80.

10. A process as in claim 1 for digesting lignocellulosic materials while retaining hemicellulose within the resulting cellulose pulp material, which comprises heating a lignocellulosic material in an alkaline cooking liquor at a digestion temperature within the range from about 100° to about 190° C. to extract substantially nondegraded hemicellulose from the lignocellulosic material and dissolve the hemicellulose in the

alkaline cooking liquor, so that the liquor contains at least about 1 percent hemicellulose having a degree of polymerization of at least 80, withdrawing at least a portion of the alkaline cooking liquor containing such dissolved substantially nondegraded hemicellulose, cooling the withdrawn liquor to a temperature below about 120° C., recycling the cooled liquor, with addition of alkali if necessary, and digesting a fresh portion of lignocellulosic material in accordance with the digestion process of claim 1 in the presence of such substantially nondegraded hemicellulose.

11. A process as in claim 10 wherein the amount of cooking liquor remaining after a portion of the cooking liquor is drawn off, is sufficient for completing the digestion of the partially cooked lignocellulosic material.

12. A process as in claim 11 wherein the amount of cooking liquor remaining is at least 1.5 liters per kg. lignocellulosic material.

13. A process as in claim 10 wherein the lignocellulosic material is birch wood and the alkaline cooking liquor containing dissolved hemicellulose is drawn off at a temperature within the range from about 130° to about 170° C.

14. A process as in claim 10 wherein the lignocellulosic material is pinewood and the alkaline cooking liquor containing dissolved hemicellulose is drawn off at a temperature within the range from about 120° to about 170° C.

15. A process as in claim 10 wherein the digestion process is carried out continuously.

16. A process as in claim 10 wherein the digestion process is carried out batchwise.

\* \* \* \* \*

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,617,431 Dated November 2, 1971

Inventor(s) Ingemar Liss-Albin Croon et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 26 : "2%" should be -- 20% --  
Column 1, line 43 : "cooling" should be -- cooking --  
Column 1, line 48 : "cooling" should be -- cooking --  
Column 4, line 64 : "dilignification" should be  
-- delignification --  
Column 6, line 58 : "NaOCL" should be -- NaOCl --

Column 8, Table I  
column headed "Mean  
Kappa Number",

line 1 - : "2" should be -- 27 --  
line 2 - : "1.3" should be -- 17.3 --  
line 4 - : "1.0" should be -- 16.0 --  
line 5 - : "2.0" should be -- 20.0 --  
line 6 - : "1.0" should be -- 16.0 --  
line 16 - : "16.9" should be -- 16.0 --  
Column 8, line 68 : "have" should be -- gave --

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Column 10, Table IV,  
column headed "Total  
lignin-free yield" -  
Run No. 7, line 40 -

: Insert -- 55.4 --

Signed and sealed this 6th day of February 1973.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents