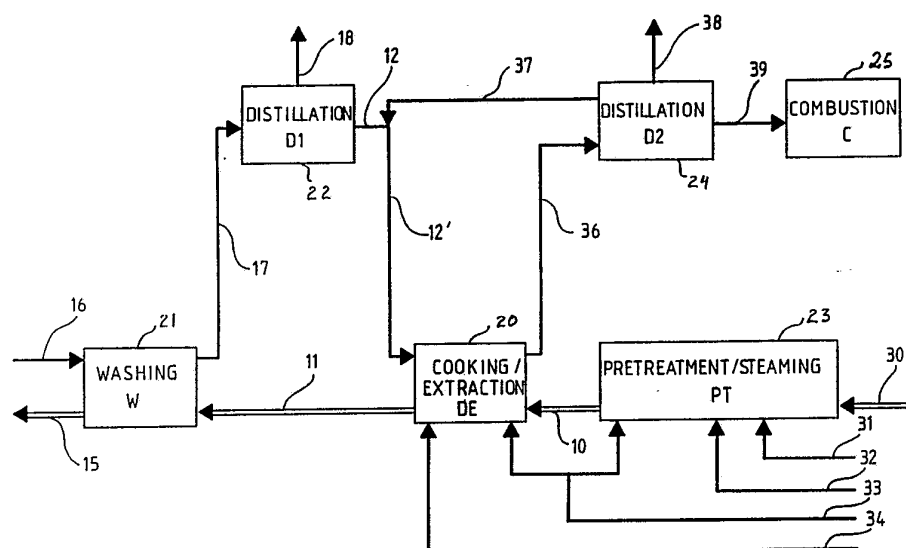




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 5 :</b>  <b>D21C 3/20</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 93/20279</b>  <b>(43) International Publication Date:</b> 14 October 1993 (14.10.93)
<b>(21) International Application Number:</b> PCT/FI93/00137 <b>(22) International Filing Date:</b> 1 April 1993 (01.04.93)  <b>(30) Priority data:</b> 863,977                      6 April 1992 (06.04.92)      US 019,113                      17 February 1993 (17.02.93)      US  <b>(71) Applicant:</b> A. AHLSTROM CORPORATION [FI/FI]; SF-29600 Noormarkku (FI).  <b>(72) Inventors:</b> EBELING, Kari ; Sateenkuja 7B, SF-02100 Espoo (FI). HENRICSON, Kaj ; Eteläpuistikatu 2 B, SF-48100 Kotka (FI). LAXEN, Torolf ; Gammelleden 13, SF-00830 Helsingfors (FI). LÖNNBERG, Bruno ; Nylandsgatan 7 B 24, SF-20500 Åbo (FI).		<b>(74) Agent:</b> A. AHLSTROM CORPORATION; Patent Department, P.O. Box 18, SF-48601 Karhula (FI).  <b>(81) Designated States:</b> BR, CA, FI, JP, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** METHOD OF PRODUCING PULP**(57) Abstract**

Solvent pulping is practised using ethanol, methanol, formic acid, or the like by passing the organic solvent countercurrent to the cellulosic fibrous material (wood) being adjusted into paper pulp. The process may be batch or continuous. The pH of the process is relatively stable and neutral, and can be controlled to maintain the process generally neutral by removing the acids formed at the beginning of the cook, e.g. with spent solvent, and can be made more uniform by adding alkali to the wood just prior to the wood coming into countercurrent contact with the organic solvent. A catalyst, such as an earth-alkali metal salt or an organic base, may also be added to the wood to enhance dissolution of the lignin. The treated pulp is washed, and the solvent in the wash liquid from the washing stage may be separated by distillation. The pulp may be steamed prior to cooking. The lignin containing liquid (spent organic solvent) may also be distilled, with the organic solvent returned to the cook, the water separated and reused, and the lignin combusted.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

## METHOD OF PRODUCING PULP

5 The present invention relates to a new method of producing chemical pulp. The invention is an improvement in solvent cooking methods (e.g. organic solvent digestion), often referred to as "solvent pulping", being generally as described in U.S. Patent No. 3,585,104.

10 Wood comprises cellulosic fibres with lignin both inside the fibres and between the fibres, bonding the fibres together. In order to carefully separate the fibres from each other, the lignin must be removed from between the fibres, the removal usually being accomplished by  
15 dissolving the lignin. Generally the cooking liquors consist of sodium hydroxide (i.e. soda cook), sodium hydroxide containing sodium sulphide (i.e. sulphate or kraft cook, also called alkaline cook), or, for example, sulphite ions (i.e. sulphite cook, also called acid  
20 sulphite cook). Lignin can also be removed by some organic solvents (hence the commercial name organosolv-process), the best known of which are methanol and ethanol. Formic acid is another proposed organic solvent.

25 Methanol and ethanol can be utilized as solvents in both alkaline and acid cooks. The advantage of acid cooks is the simple recovery of the chemicals, as wood contains acids that make the cook acid, when only methanol or ethanol are used as solvents. The disadvantage of acid  
30 cooks is the poor quality of the produced pulp, because the cellulosic fibres will, to some extent, degrade in acid treatment. In alkaline cooks the quality of the produced pulp will remain good, but the problem in alkaline cooks is the recovery of chemicals. Some alkali,  
35 mostly a sodium-based alkali, will firstly have to be added into the cook and then recovered and used again. A known alkaline organic solvent process is the "Organo-cell-process", presently being used in Germany, in which process the cook is a soda-methanol cook.

According to the present invention, it has been determined that during solvent pulping acids are formed in the very beginning of the cook. The pH of the cook can be kept in the desirable range (generally neutral) by removing the acids from the beginning of the cook, i.e. almost immediately after they are formed. By keeping the pH generally neutral, the pulp quality is enhanced, both for continuous and batch cooking processes. This is accomplished, in general, by countercurrent flow during continuous cooking, and in batch cooking by withdrawing solvent from the batch digester after a predetermined time from the start of the cook (and perhaps periodically thereafter), while the cook continues after the solvent withdrawal, with new solvent added.

According to one aspect of the present invention there is provided a method of producing cellulose pulp from comminuted cellulosic fibrous material by organic solvent pulping comprising the step of (a) controlling the pH of the material during cooking so that it is generally neutral by removing acids formed at the start of the cook together with organic solvent used in the cook and by adding alkali to the cellulosic fibrous material in an amount sufficient to maintain the pH at the desired value. This method may be practised utilizing a treatment vessel, comprising further the further steps of: (b) Causing the cellulosic fibrous material to flow in a first direction into the treatment vessel, and to be removed from the treatment vessel in the same, first, direction, whereby the needed amount of alkali is added to the material prior to the treatment vessel; and (c) introducing an organic solvent containing liquid stream to dissolve the lignin of the cellulosic fibrous material into the treatment vessel in a second direction, opposite the first direction. Step (a) is practised by removing the acids formed during pulping, together with spent organic solvent, from the treatment vessel.

According to another aspect of the present invention, there is provided a method of producing cellulosic pulp from comminuted cellulosic fibrous material by solvent pulping comprising the steps of:

5 causing the comminuted cellulosic fibrous material to flow in a first stream in a first direction;

causing a stream of organic solvent to flow into operative contact with the comminuted cellulosic fibrous material countercurrent to the first stream, that is in a  
10 second direction, opposite the first direction throughout the area of operative contact between them, which causes organic acids to be produced as the organic solvent dissolves the lignin from the cellulosic fibrous material; and

15 removing organic acids formed during solvent pulping from intimate contact with the cellulosic fibrous material along with the countercurrent flow of organic solvent.

It is the primary object of the present invention to  
20 provide effective solvent pulping with a stable pH. This and other aspects of the invention will become clear from an inspection of the detailed description of the invention, and from the appended claims.

25 The method of producing pulp according to the invention will become clear from the detailed description, with reference made to the accompanying drawings, of which:

30 Figure 1 is a schematic of an exemplary embodiment of a cook/extraction process according to the invention;

Figure 2 is a schematic of another exemplary embodiment of a cook/extraction process according to the  
35 invention;

Figure 3 is a schematic of an exemplary embodiment of the washing stage subsequent to the cook/extraction process;

5        Figure 4 is a schematic of an exemplary embodiment of solvent recovery process according to the invention;

10        Figure 5 is a schematic of another exemplary embodiment of a cook/extraction process according to the invention;

15        Figure 6 and 7 illustrate the change of pH as observed when examining the cook/extraction process of Figure 1;

Figure 8 is a schematic diagram illustrating apparatus for practising a method according to the present invention;

20        Figure 9 a schematic of an exemplary embodiment of solvent and alkali recovery process according to the invention; and

25        Figure 10 is a possible process alternative of an application of the invention; and

Figure 11 is a possible process alternative of an application of the invention on an industrial scale.

30        Figure 1 illustrates a schematic representation of the principle of a countercurrent cook/extraction treatment vessel/stage 20 according to the invention. The number 10 refers to comminuted cellulosic fibrous material (e.g. wood) being fed into the process and the number 11  
35        refers to cellulosic fibres of the wood, produced by dissolving and extracting lignin from the wood. The number 12 refers to the organic solvent being fed to the process

and the number 13 refers to the spent organic solvent being exhausted from the process, with dissolved lignin also present. The process of Fig. 1 was examined in laboratory conditions with the surprising result shown in Fig. 6.

5  
10  
15  
In a normal organosolv cook of softwood the pH followed the curve 100. As the acids in the wood are dissolved the pH decreases in about 15 minutes to 3.6 - 3.5 and remains at this level for the rest of the cook. In a organosolv cook of hardwood, the pH decreases to 3.8 - 4.0. This means that all acids either form or dissolve in the initial phase of the cook. The poor fibre strength produced is due to the acid conditions in the cook. The low pH in the cook of softwood may also result in condensation of lignin which prevents dissolution of lignin.

20  
25  
30  
In a countercurrent organosolv cook according to the present invention the pH followed the curve 101. In the initial stage of the extraction the pH was noticed to decrease sharply, but then to quickly increase to almost the original level of about 5.5. The reason for this must be that the organic acids present in the wood are initially dissolved into the solvent, and as the process is a countercurrent one, the acids are washed away with the solvent during the later stages of the cook. The pH can be maintained on an almost neutral level during the cook without using alkali. The quality of the pulp is improved because of reduced acidity during the later stages of the cook.

35  
In 1989, at the Solvent Pulping Conference, Quinde gave a lecture on what happens to the extractives of pine in a methanol cook (80% methanol, 205 °C). He concluded, that 90% of resin acids and about one fourth of fatty acids are dissolved during the first five minutes. This supports the surprising result that the fall of the pH can

be prevented by countercurrent flow of cooking liquor, as shown in Fig. 6 (or by removing the formed acids shortly after production in a batch digester). Obviously the remaining resin and fatty acids are removed due to the countercurrent nature of the process. Thus, according to the invention, the pH of the extraction process can be controlled by removing the organic acids, formed during the process, together with the always countercurrent flow of solvent.

The results from the experiments described in Fig. 6 can be further explained by means of Fig. 7.

On region C of Fig. 7 the pH is below 4.5 whereby the quality of the pulp deteriorates. In the case of a normal ethanol cook most of the time the pH is below this level and this results in poor quality of pulp. This case is represented by curve 104 in Fig. 7. However, when utilizing a countercurrent cooking procedure as according to the invention, the pH remains below the minimum desirable level (line 105) for pH during the cook only a short period of time. Since the time during which the pH is too low is short, a pulp of good quality is produced. This is represented by curve 103 in Fig. 7.

The pulp quality can be further improved by adding alkali to the countercurrent cook at the beginning of the cook. This case is shown in Fig. 7 by curve 102. The alkali added in the beginning increases the pH and acids formed or dissolved neutralize the cook and the pH decreases to an almost neutral value during the countercurrent cook. There is a maximum desirable pH, represented by line 106, which is desirably not exceeded (region A in Fig. 7) because then the amount of alkali that has to be recovered becomes so high that the recovery system becomes expensive. By controlling the pH in this way within region B, a pulp of good quality is produced.



It can be said that it is most advantageous to keep the pH of the solvent cooking process in the range of 4.5 - 12, but it can be momentarily allowed to decrease below 4.5 or increase above 12 at the beginning of the cook. The minimum is reached when no alkali is used and the maximum when alkali is used. Alkali can also be added in such an amount as to maintain the pH of the cook between the minimum and maximum limits.

10 A countercurrent extraction according to Fig. 2 ensures that the pH does not decrease at the initial stages of the cook/extraction 20. An addition of alkali 14, for example  $\text{CaO}$ ,  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$ , or a combination thereof, to the wood material 10 being fed into the cook, 15 neutralizes the initial stage of the cook and so prevents the pH from falling. Thus the pH is prevented from decreasing to the level of about 3-4, where hydrolysis would degrade the cellulosic fibres. The amount of acid forming at the initial stages of the cook is 8-20 kg/ton 20 of pulp, and an amount of alkali corresponding to the amount of acid is added, if the pH is to be kept out of the acid range (e.g. generally neutral, for example a pH of about 6.5 - 7.5). Due to the essentially completely countercurrent nature of the cook there is some alkali 25 present at the initial stages of the cook 20, but it is then washed away and removed with the dissolved lignin in stream 13.

When effecting countercurrent cooks in laboratory 30 conditions it was also discovered that a high ethanol or methanol content (e.g. 70% or more) in the organic solvent containing liquid gives a better delignification result. It has usually been presumed, that due to the water included in the wood, the ethanol content could be 50% at 35 the most. When a countercurrent cook is effected, the ethanol content can be substantially increased to exceed 50% of the organic solvent containing liquid by maintain-

ing a high ethanol content in the inlet streams 12 (Figs. 1 and 2). According to the invention, the water is washed away at the beginning of the cook and is removed with streams 13. Thus the countercurrent cook gives a possibility of both controlling the pH and increasing the content of the organic solvent.

The residual solvent in the stream of fibres subsequent to the extraction 20 must be washed away as shown in Fig. 3. The stream 11 of fibres is a mixture of organic solvents and wood fibres. Because of the countercurrent nature of the cook/extraction, it can be presumed that the fibres are suspended in nearly pure solvent. In the washing stage 21 the solvent is washed away with washing liquid 16, mostly water. The result is a wood fibre-water suspension 15 and a solution 17 of water and solvent, mostly a mixture of water and ethanol or methanol.

The solvent is recovered from stream 17 by a process according to, for example, Fig. 4. The solution 17 of water and solvent is directed to distillation apparatus 22, where the water 18 and solvent 12 are separated. The solvent 12 is directed to cook 20. As is shown in Fig. 4, it is possible to effect a wash in 21 with water and still maintain a high ethanol and/or methanol content in the actual cook 20. The pulp, if any, still in the form of chips prior to the wash, is fiberized prior to the wash to optimize the wash. The organic solvent 12 preferably has a substantially greater than 30% methanol and/or ethanol content.

Fig. 5 illustrates a process more developed than heretofore described. The wood 30 introduced into the process is heated at the beginning of the cook by feeding steam 31 in the wood material in presteamer 23. Alkali 32 is at the same time introduced into the wood material to increase the pH at the initial stage of the cook. A

catalyst 33 can be introduced during either the pretreatment 23 or at the beginning of the cook 20 to enhance the dissolving of lignin. A commonly used catalyst in acid process is  $\text{CaCl}_2$ . The  $\text{Ca}^{2+}$  ions are advantageous to the process, but on the other hand the amount of acid is detrimentally increased in the reaction  $2\text{Cl}^- + 2\text{H}^+ \rightarrow 2\text{HCl}$ . Organic bases, such as amine, can be used as catalysts in acid, neutral and alkaline processes. Ethanol or methanol 34 is added to make up for the losses of solvent in the process.

The process has further been complemented by treatment of the lignin-containing outlet liquid 36. Naturally, the outlet liquids 13 of the previous embodiments can also be treated accordingly. The outlet stream 36 of solvent from the cook 20 mostly contains solvent, polysaccharides, lignin and water. The mixture 36 is directed to distillation/evaporation stage 24, where the solvent, mostly ethanol and/or methanol 37, is separated from the water 38 and lignin and polysaccharide material 39. The solvent 37 can be returned to the cook 20 together with the solvent 12 from the distillation stage 22, while the water and lignin material are directed to combustion apparatus 25 or other treatment device. One possibility is to separate the lignin and to produce, for example, vanillin from the separated lignin. The added alkali 32, if any, is directed to combustion apparatus 25 and can thereafter be reused, or, if desired, removed. Removal is typically practised if the amount of the added alkali is small, e.g. 10-50 kg/ton of pulp.

In a laboratory test producing pulp of good quality,  $\text{CaCl}_2$  was utilized as catalyst, the amount of which was 5-50 g/l (that is about 5-50 grams of catalyst per litre of material being treated). The temperature of the cook was 195 °C and the duration of the cook 20 was 3 hours. Other possible catalysts, besides  $\text{Ca}^{++}$ , are  $\text{Mg}^{++}$  and  $\text{Na}^+$ . For

the lignin extraction it is advantageous that the wood is impregnated with alkali (14, 32), as this causes the wood to swell and thereby improves the extraction of lignin.

5           Ethanol is probably a better solvent than methanol for the practice of the invention, but the deacetylation that occurs in the wood produces some methanol. Thus there is always some methanol present in the process, even if the only fresh solvent 34 is ethanol.

10

          The invention can be applied to numerous cooks, both batch cooks and continuous cooks. The invention can, for example, be utilized in continuous digesters with a pretreatment zone or in continuous digesters with a  
15       separate pretreatment vessel. When the invention is practised with batch digesters, the acids produced at the beginning of the cook can be removed by withdrawing solvent from the digester after a predetermined time (e.g. about 5 - 10 minutes, but dependent upon material being  
20       cooked, the exact composition of the organic solvent, etc.) - the produced acids being removed with the solvent - and introducing at least some new solvent. While normally not necessary since most of the acids are produced within the first five minutes or so, the with-  
25       drawal and replacement procedure can be practised periodically if desirable. The pH during batch cooking can alternatively, or in addition, be maintained generally neutral during the initial stages of the cook by adding alkali to the material prior to or simultaneously with  
30       introduction into the digester.

          The invention may be further illustrated by the following examples.

35       Example

A series of laboratory tests on softwood were performed to study the method. In laboratory the organosolv cooking process was performed as follows:

5      Step 1:

10      The chips were pretreated in a pretreatment liquor consisting of NaOH dissolved in water. The pretreatment time was about 30 minutes and the temperature 120 °C. The idea of the pretreatment step was to cause the fibre to swell so as to enhance the subsequent ethanol extraction step. Another reason for the pretreatment step was to enable the addition of alkali to the chips to keep the pH at a sufficiently high level during the rest of the cook.

15      During the pretreatment step the amount of alkali was varied between 0.25 to 1.50 mol NaOH/l. It was found that when the amount of alkali was below 0.25 mol NaOH/l the delignification was insufficient and the amount of unfiberized wood high. At alkali levels above 1.00 mol NaOH/l the yield loss in the cook became too high. Probably the amount of alkali actually needed depends on type of wood used. For the tested Scandinavian spruce the optimal alkali level was between 0.5 and 1.0 mol NaOH/l.

25      Step 2:

The chips were removed from the pretreatment liquor by lifting the chips out. It was found that about 30 - 70 kg of NaOH per ton of pulp was entrained with the chips.

30      Alkali had also been consumed in the pretreatment vessel. The consumption was 50 - 300 kg NaOH per ton of pulp.

Step 3:

35      Subsequent to steps 1 and 2 the chips were taken to a countercurrent ethanol extraction step. The duration of this solvent extraction step was about 120 minutes and the

temperature 185 °C. Anthraquinone was added to the solvent to improve delignification. The added amount of anthraquinone was between 0 and 1.0 mmol.

5           The strength of the ethanol solvent was varied between 25% and 100%. The lowest residual lignin contents were achieved when the ethanol content was between 40 and 70% in the liquid phase. When being tested for bleachability and pulp properties, the pulp was found to have  
10           pulp properties close to those of kraft pulp regarding both bleachability and strength.

          Figure 8 shows an apparatus with which the process of example 1 can be performed. The apparatus comprises a  
15           conventional chips bin 201 connected by a conventional low pressure feeder 202 to a conventional horizontal steaming vessel 203, which in turn is connected by a conventional chute 203 to a conventional high pressure feeder 204. Wood chips are first steamed and preheated and then taken  
20           through the first pressure feeder 204 in line 205 to the pretreatment vessel 206 in which the chips are treated in an alkaline solution. The alkaline solution is introduced into the system in line 207. A conventional liquid/  
25           material separator system is provided at the top of the vessel, with withdrawn liquid recirculated via line 208 to the inlet high pressure port of the feeder 204. The alkali can come from one or several of the following sources:

30           - waste water from alkaline bleaching stages, for example, E or P stages;

          - NaOH, either brought fresh to the mill or manufactured at the mill by causticizing  $\text{Na}_2\text{CO}_3$ ; and/or

35           -  $\text{Na}_2\text{CO}_3$  if the alkalinity needed is so low that only part of the alkali must be NaOH.

From the pretreatment vessel 206 the chips are taken to the extraction zone 215 in the second pressure vessel 213 in which the pressure is much higher than in pressure vessel 206. The chips material passes via line 211 to the top of the vessel 213 from a high pressure feeder 209 in the bottom of the pretreatment vessel 206. A conventional liquid/material separator system is provided at the top of the vessel 213, with withdrawn liquid recirculated via line 212 to the inlet high pressure port of the feeder 209. In order to control the temperature of the recirculating liquid so as to minimize the possible adverse effects on the high pressure feeder 209, the liquid is passed through a heat exchanger 210.

The second vessel 213 preferably consists of two zones: (1) zone 215 in which the chips are extracted with ethanol/methanol; and (2) zone 216 in which the chips are washed before being discharged from the vessel.

Filtrate from a subsequent washing or bleaching step is used as washing liquid. The washing liquid is introduced into the bottom of the vessel 213 through line 218. The pulp at the bottom of the vessel 213 is washed and discharged into line 219.

The ethanol and/or methanol is added at a point above the washing zone 216 in line 217. The ethanol is introduced at such a strength and amount that optimal extraction conditions are achieved in the extraction zone 215. If necessary, water can be separated from the circulation 220 by distillation to control methanol/ethanol strength in the extraction zone 215.

The extraction liquor is withdrawn from the extractor/digester 213 into a withdrawal conduit 214. The withdrawn liquor containing the alkali used, the ethanol/-

methanol used and the dissolved lignin, is taken to recovery.

5 A simplified recovery system for solvent and alkali is shown in Fig. 9. The extraction liquor 214 from Fig. 8 is treated in the following steps: (a) Ethanol/methanol separation (250). The solvent is then reused in the extraction vessel 213. (b) Evaporation (252) in which water is separated. (c) Combustion (254) of lignin and  
10 polysaccharides.

During combustion, a melt (255) consisting essentially of  $\text{Na}_2\text{CO}_3$  is produced. This melt is dissolved in water and used as a  $\text{Na}_2\text{CO}_3$  containing liquid in the pretreatment  
15 vessel 206 or causticized to NaOH before using in the pretreatment vessel 206. If the  $\text{Na}_2\text{CO}_3$  amount is small it does not have to be reused.

If the produced pulp is to be chlorine free, the pulp  
20 can be bleached with oxygen, ozone and peroxide. Fig. 10 illustrates a diagram of a process in which the initial bleaching is effected by oxygen and the actual final bleaching by ozone and peroxide.

25 In the system of Fig. 10, the wood chips 300 that are introduced into the process are first heated by feeding steam 301 to the wood material to a pretreatment vessel 323. Alkali 302 is at the same time introduced into the wood material so that the chips are treated at a pH of 11  
30 - 12. The alkali is obtained from the bleach plant effluents, which contain 40 - 120 kg of NaOH/adt. If the volume of the effluent is too big, the effluent has to be evaporated in order to reduce the volume. Additional alkali is brought if needed in the form of NaOH or  $\text{Na}_2\text{CO}_3$ .

35

After pretreatment 323 the chips 310 are introduced to the extraction stage 320 where some methanol and/or



ethanol 312' may be added in the beginning to control the liquor- to - wood ratio, or to increase the content of methanol/ethanol in the beginning of the extraction process 320.

5

After extraction the chips 311 are washed with the bleach plant effluents 302', 303, 304, which may be acid or alkali depending on how the bleaching has done. If possible, the acid filtrates 303 and 304 are used in the washing 321 and the alkali filtrate 302 in chips pretreatment 323. The washing liquid 317 containing solvent may have to be strengthened by distillation 322 before adding methanol and/or ethanol 312 to the extraction stage 320.

10

The pulp 315 from the washing stage is introduced into the bleach plant 330 in which the pulp is bleached in the sequence OZP.

15

After the extraction stage 320 the waste liquor 306 is recovered, evaporated and combusted. If the alkali amount is low, the  $\text{Na}_2\text{CO}_3$  formed in the recovery process is removed from the mill and fresh NaOH is brought in. Some of the  $\text{Na}_2\text{CO}_3$  may be used in the pretreatment stage. If the amount of alkali in the effluent stream is large it is probably more practical to causticize the formed  $\text{Na}_2\text{CO}_3$  to NaOH and thus generate new NaOH for bleaching and pretreatment at the mill.

20

25

#### Example

In one successful test, the wood was pretreated with a mixture of 75 %  $\text{Na}_2\text{CO}_3$  and 25 % NaOH in amount that corresponds about 200 kg Na/adt expressed as NaOH. This means that about 50 kg/adt of NaOH was used and the rest was  $\text{Na}_2\text{CO}_3$ .

30

35

The amount of NaOH needed in the bleaching sequence OZEP is also about 50 kg/adt. Thus all alkali needed in

the pretreatment of the chips in the form of NaOH is received from the bleach plant effluent water. The rest of the alkali can be used as  $\text{Na}_2\text{CO}_3$  which is the form of the Na when burning the residual liquor in a recovery boiler.

5

Thus, a mill does not need any causticizing plant, but uses  $\text{Na}_2\text{CO}_3$  from the combustion of spent liquor and NaOH from bleach plant effluents.

10

Filtrates from the bleach plant can be used to dissolve the  $\text{Na}_2\text{CO}_3$  from the recovery boiler thus further reducing the water effluent volume.

15

Fig. 11 also illustrates a schematic technical diagram of a process in which the initial bleaching is effected by oxygen and the actual final bleaching by ozone and peroxide.

20

While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiment, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

25

## WHAT IS CLAIMED IS:

1. A method of producing cellulose pulp from comminuted cellulosic fibrous material by organic solvent pulping, **characterized** in that said method comprises the step of (a) controlling the pH of the material during cooking so that the pH is generally at least neutral by removing acids formed at the start of the cook together with organic solvent used in the cook and by adding alkali to the cellulosic fibrous material in an amount sufficient to maintain the pH at the desired value.

2. A method according to claim 1, wherein a treatment vessel is utilized, **characterized** in that said method comprises the further steps of:

(b) causing the cellulosic fibrous material to flow in a first direction into the treatment vessel, and to be removed from the treatment vessel in the same, first, direction, whereby the necessary amount of alkali is added to the material prior to the treatment vessel; and

(c) introducing a stream of liquid containing organic solvent to dissolve the lignin of the cellulosic fibrous material into the treatment vessel in a second direction, opposite the first direction; and wherein step (a) is practised by removing the acids formed during pulping, together with spent organic solvent, from the treatment vessel.

3. A method according to claim 2, **characterized** in that steps (b) and (c) are practised substantially continuously, and wherein extraction of spent organic solvent in step (a) also is practised continuously, substantially in the second direction.

4. A method according to claim 2, **characterized** in that said method comprises the further step of treating

the extracted spent organic solvent to remove organic solvent from the dissolved material therein.

5 5. A method according to claim 4, **characterized** in that said method comprises the further step of introducing the separated organic solvent from the separation step to be used as organic solvent in step (b).

10 6. A method according to claim 4, **characterized** in that said method comprises the further step of combusting the separated material removed from the organic solvent in the separation step to produce a melt containing  $\text{Na}_2\text{CO}_3$  and of dissolving the melt in water to produce a liquid, which is used in step (b) without or after causticization.

15 7. A method according to claim 2, **characterized** in that the treatment vessel is a continuous digester, and that the treated cellulosic fibrous material removed from the treatment vessel in the first direction is subjected to washing to effect removal of undesired chemicals therefrom.

20 8. A method according to claim 7, **characterized** in that some of the chemicals removed during washing comprise organic solvent, which is separated from the washing liquid and introduced into the treatment vessel in step (b).

30 9. A method according to claim 8, **characterized** in that the organic solvent is separated from the washing liquid by distillation.

35 10. A method according to claim 2, **characterized** in that said method comprises the further step of steaming the cellulosic fibrous material prior to introducing it into the treatment vessel in step (a).

11. A method according to claim 2, **characterized** in that said method comprises the further step of introducing a catalyst to enhance dissolving of lignin into the cellulosic fibrous material prior to the introduction thereof into the treatment vessel.

12. A method according to claim 11, **characterized** in that the catalyst is selected from the group consisting essentially of salts of alkali-earth metals, anthraquinone and organic bases, and wherein said step of adding catalyst is practised to add about 5-50 grams of catalyst per litre of material being treated.

13. A method according to claim 1, **characterized** in that step (a) is practised in a batch digester by removing spent solvent containing formed acids, from the digester shortly after formation of the vast majority of acids at the start of the cook.

14. A method according to claim 1, **characterized** in that the organic solvent in the organic solvent containing liquid is selected from the group consisting essentially of methanol, ethanol, and mixtures of methanol and ethanol.

15. A method according to claim 14, **characterized** in that the amount of methanol, ethanol, and mixtures of methanol and ethanol, is substantially greater than 50 % of the total amount of the solvent containing liquid.

16. A method of producing cellulosic pulp from comminuted cellulosic fibrous material by solvent pulping, **characterized** in that said method comprises the steps of:  
causing the comminuted cellulosic fibrous material to flow in a first stream in a first direction;

causing a stream of organic solvent to flow into operative contact with the comminuted cellulosic fibrous

material countercurrent to the first stream, that is in a second direction, opposite the first direction throughout the area of operative contact between them, which causes organic acids to be produced as the organic solvent dissolves the lignin from the cellulosic fibrous material; and

removing organic acids formed during solvent pulping from intimate contact with the cellulosic fibrous material along with the countercurrent flow of organic solvent.

17. A method according to claim 16, characterized in that said method comprises the further step of introducing alkali into the stream of comminuted cellulosic fibrous material adjacent the area where it first comes in contact with the cellulosic fibrous material in an amount sufficient to neutralize the slurry of organic solvent, the cellulosic fibrous material, and other constituents, at that area and to swell the fibre layers in order to improve the alcohol penetration.

18. A method according to claim 17, characterized in that said method comprises the further step of introducing a lignin dissolving enhancing catalyst into the cellulosic fibrous material prior to its being brought into contact with organic solvent.

19. A method according to claim 16, characterized in that the organic solvent is part of an organic solvent containing liquid.

20. A method according to claim 19, characterized in that the amount of organic solvent in the organic solvent containing liquid is substantially greater than 50% of the total amount of the solvent containing liquid.

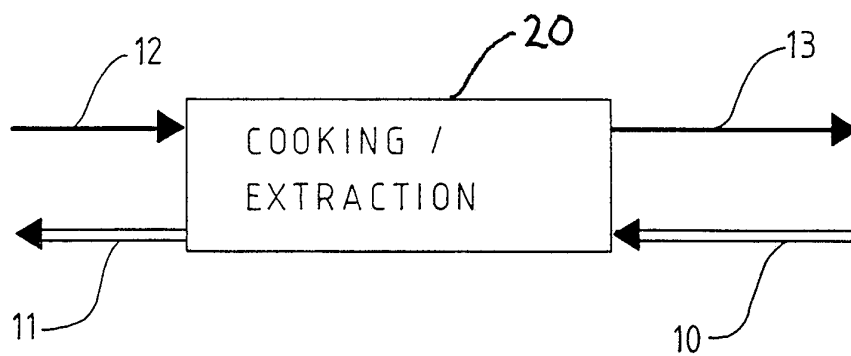


FIG. 1

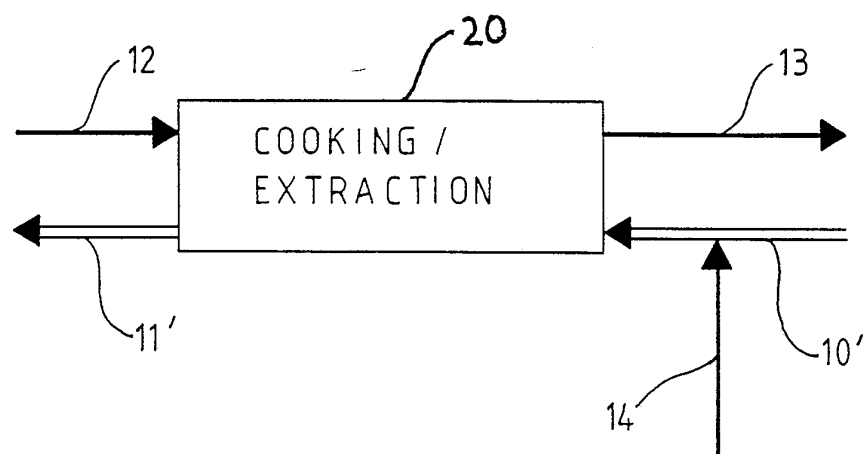


FIG. 2

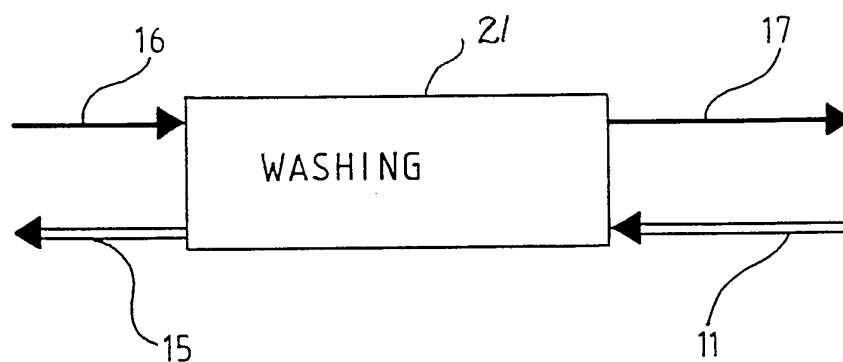


FIG. 3

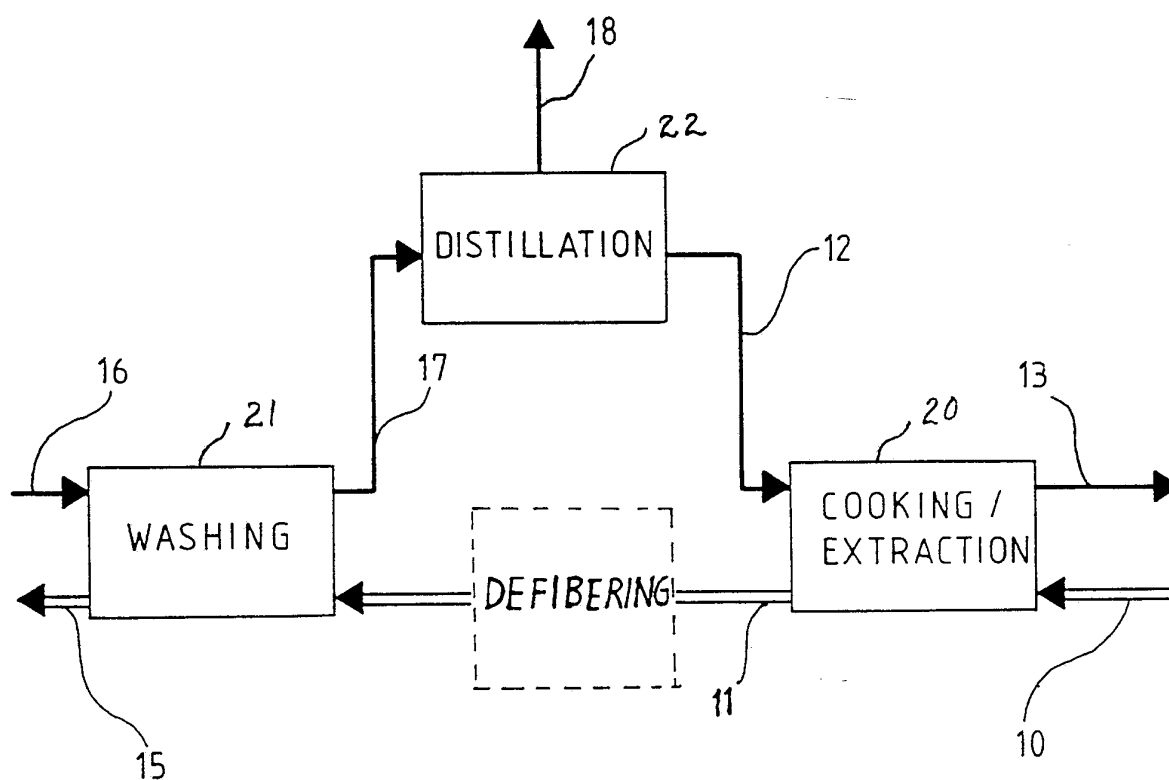


FIG. 4



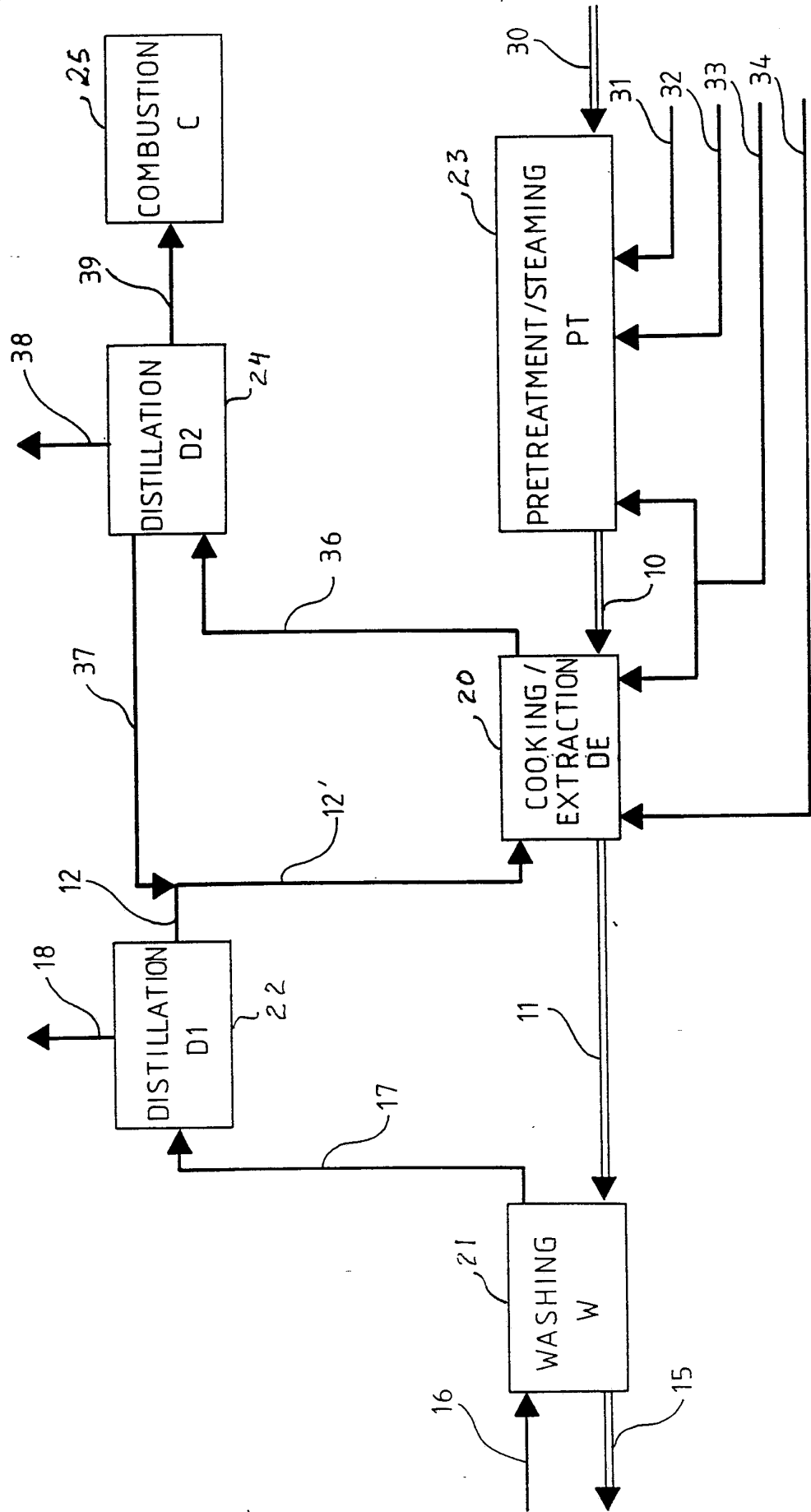


FIG. 5

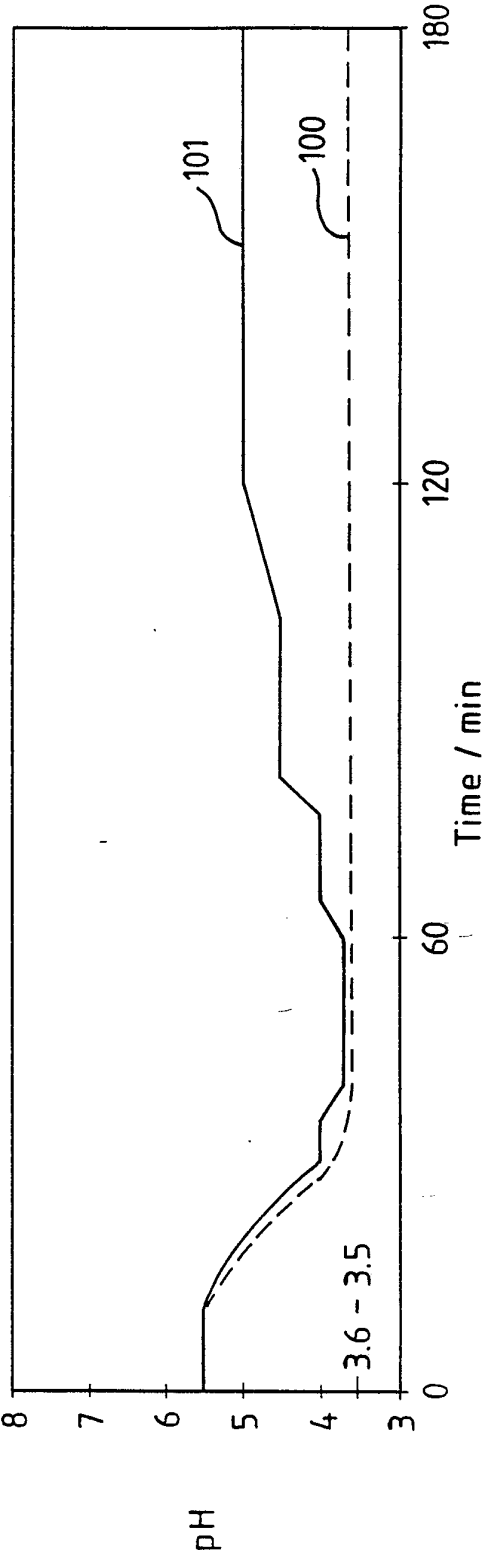


FIG. 6

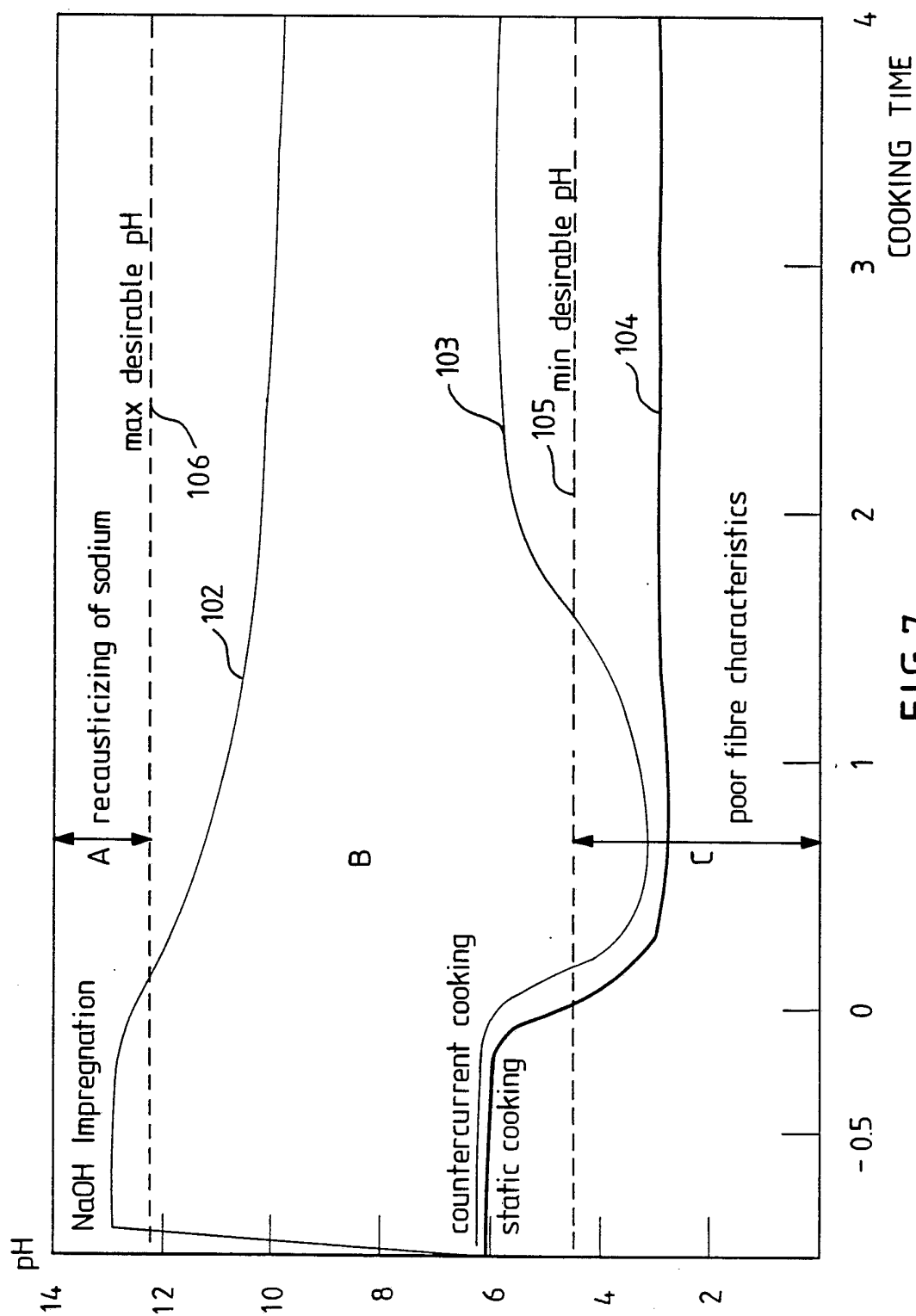


FIG.7

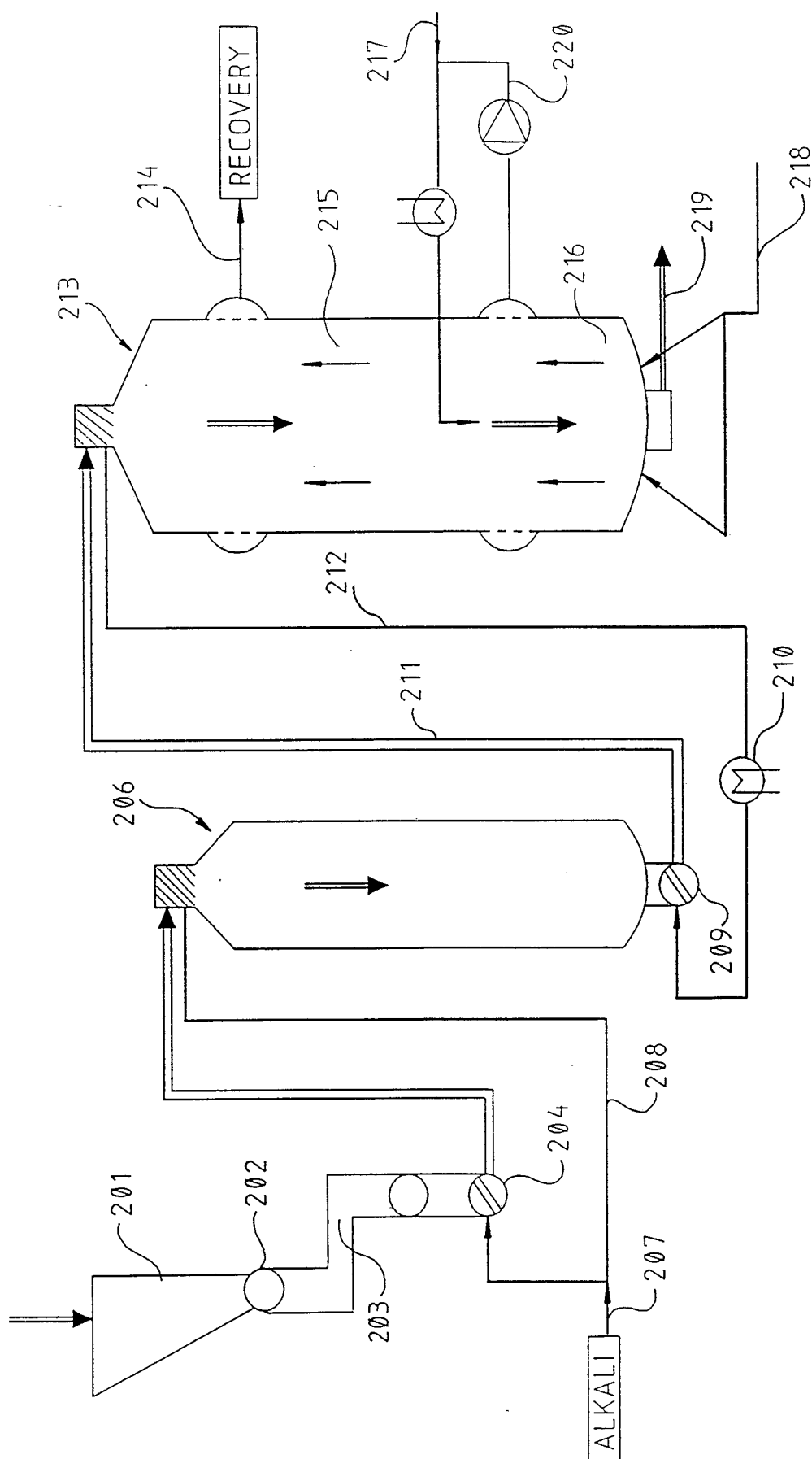


FIG. 8

7/9

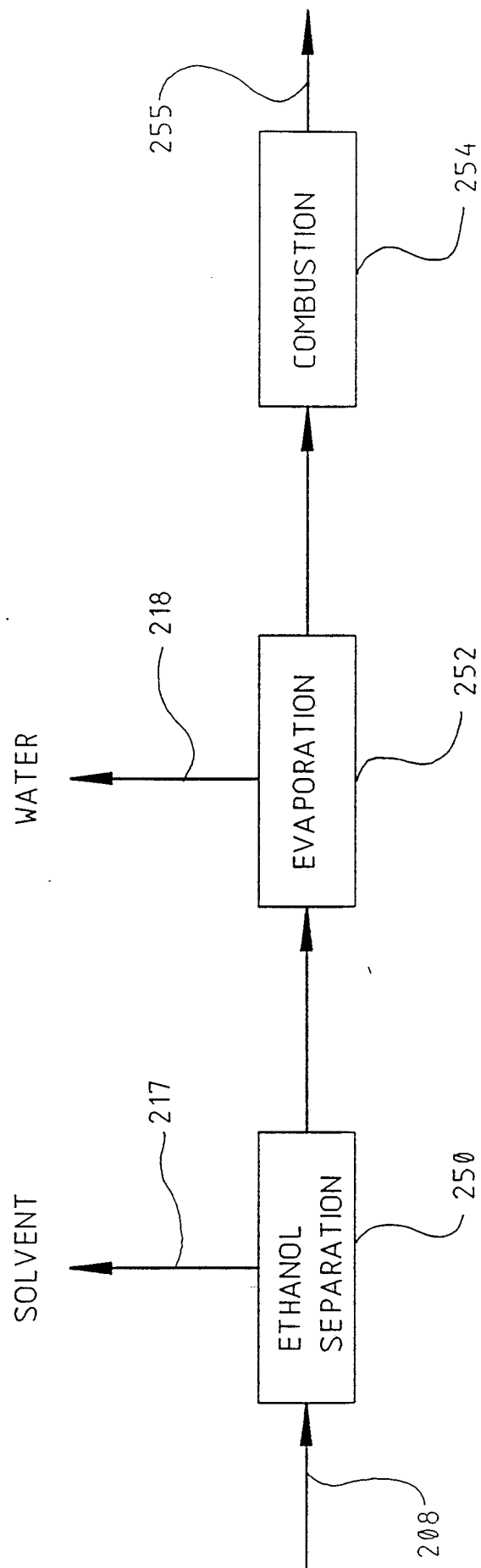


FIG. 9

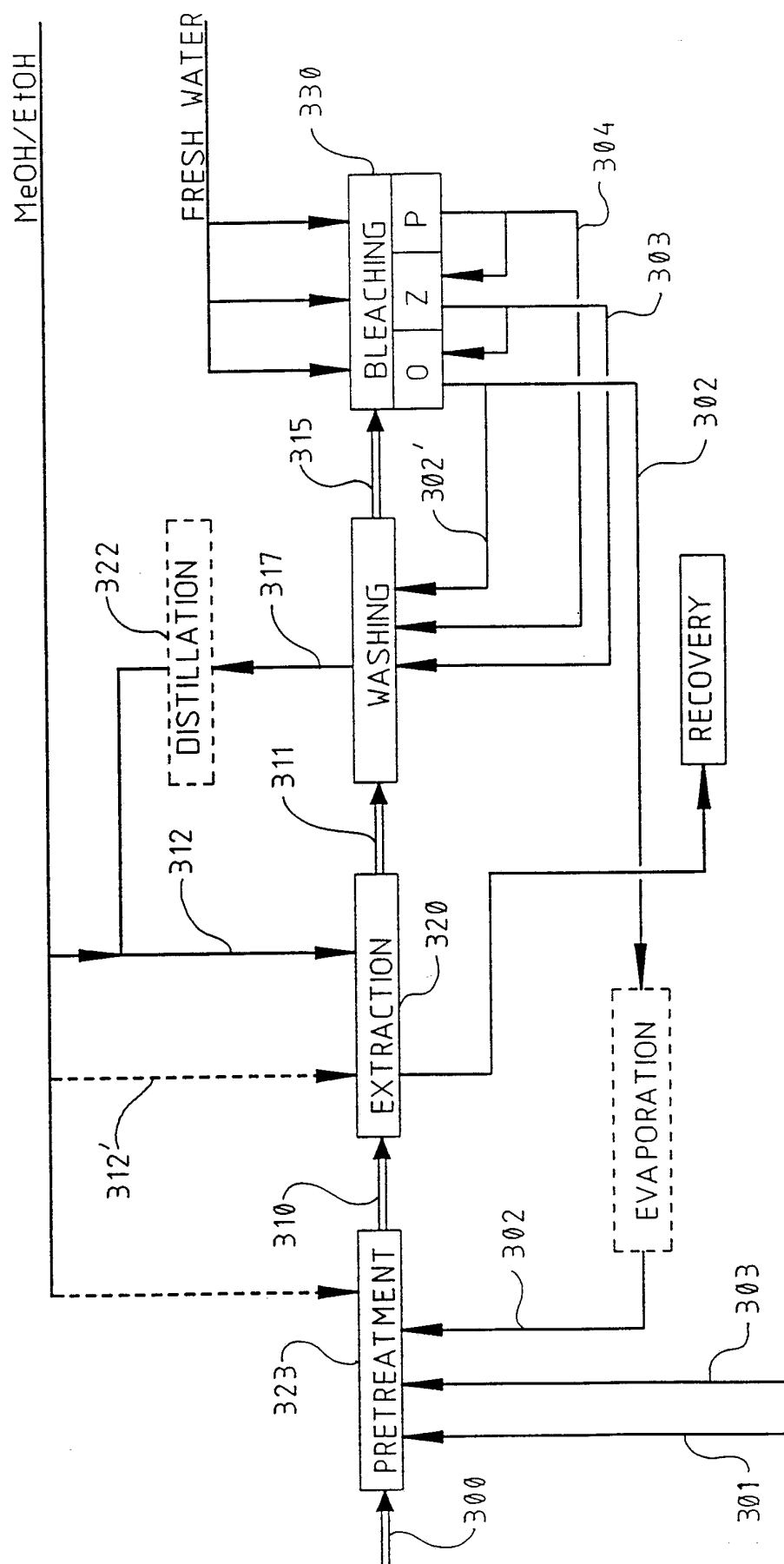
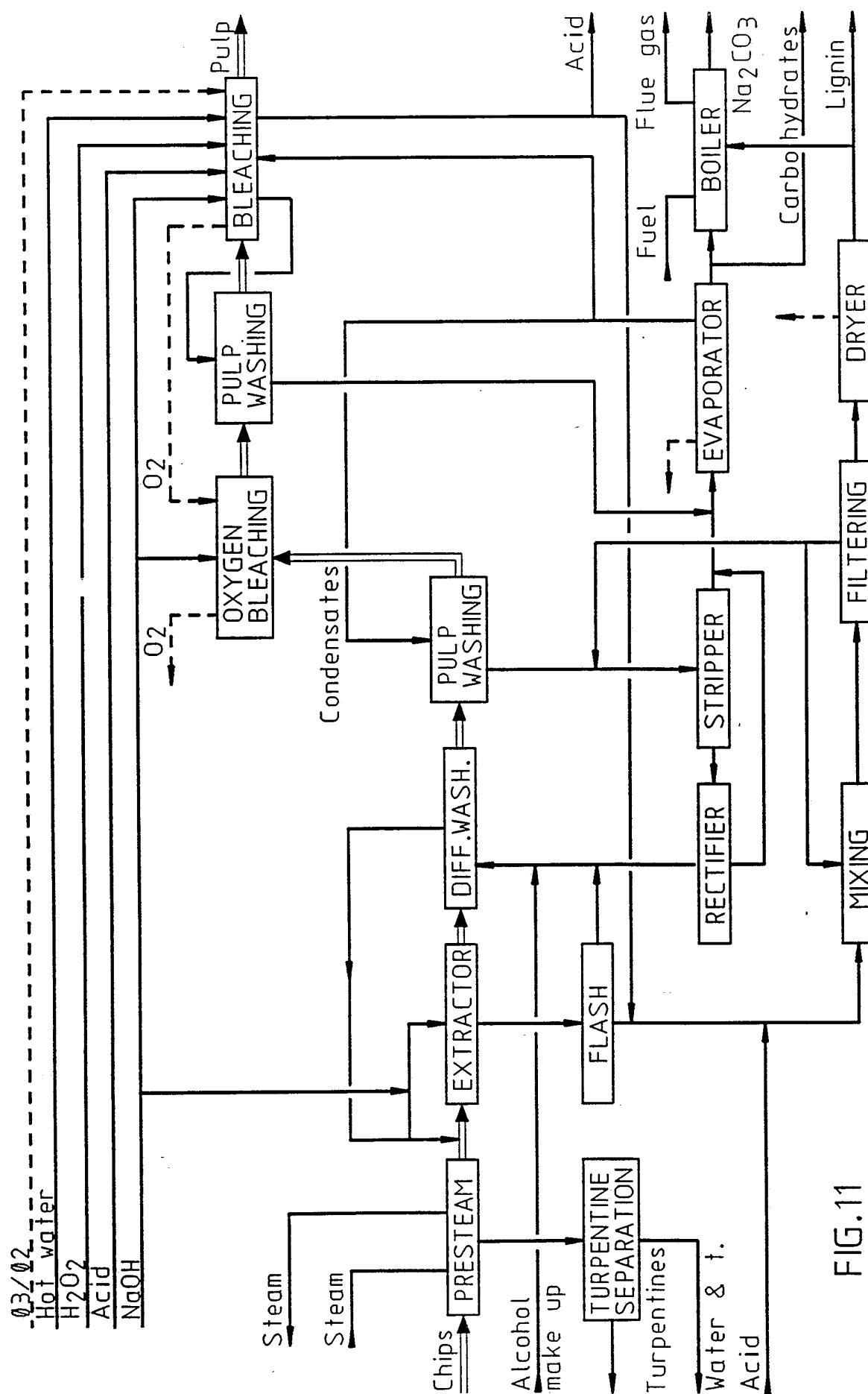


FIG. 10



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 93/00137

## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: D21C 3/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE, B1, 2644155 (KLEINERT, THEODOR N.), 1 December 1977 (01.12.77), column 2, line 28 - column 4, line 6	1, 14-17, 19-20
Y	--	18
Y	WO, A1, 8200483 (BAU- UND FORSCHUNGSGESELLSCHAFT THERMOFORM AG), 18 February 1982 (18.02.82), claim 1	18
A	--	11-12

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

29 June 1993

Date of mailing of the international search report

09 -07- 1993

Name and mailing address of the ISA/

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Marianne Bratsberg

Telephone No. +46 8 782 25 00



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 93/00137

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3585104 (T.N. KLEINERT), 15 June 1971 (15.06.71), column 2, line 65 - column 3, line 24  -----	7-10

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

28/05/93

International application No.  
PCT/FI 93/00137

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-B1- 2644155	01/12/77	AT-B- 364240 JP-A- 53061702 SE-B,C- 434961 SE-A- 7710907	12/10/81 02/06/78 27/08/84 31/03/78
WO-A1- 8200483	18/02/82	CA-A- 1150012 EP-A,B- 0056409 SE-T3- 0056409	19/07/83 28/07/82
US-A- 3585104	15/06/71	NONE	