

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **87311493.8**

(22) Date of filing: **29.12.87**

(51) Int. Cl.4: **D 21 C 9/02**
D 21 C 3/04, D 21 C 1/04,
D 21 C 11/00

(30) Priority: **31.12.86 FI 865360**

(43) Date of publication of application:
06.07.88 Bulletin 88/27

(84) Designated Contracting States: **AT DE FR IT SE**

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(54) **Procedure for recirculating phenol in a lignocellulosic materials digestion process.**

(57) A process for recirculating phenol in a lignocellulosic materials digestion process in which lignocellulosic material is digested with phenol-containing solutions in order to dissolve lignin, characterised in that phenol recirculation is carried out as a cyclic process in which the phenol-containing solution is first used in the washing of the cellulosic material from the phenol digeston, thereafter in the lignocellulosic material digestion step, and finally in a lignocellulosic material impregnation step preceding the phenol digestion process.

Description

Procedure for recirculating phenol in a lignocellulosic materials digestion process

The present invention concerns recirculation of phenol in a lignocellulosic materials digestion process.

5 The use of phenol and other phenolic compounds towards separating lignin from wood is known in the art. For state of technology, for instance the references Schweers, Chemtech 1974, 491 and Applied Polymer Symposium 28, 277 (1975) are cited. Briefly described, the procedure comprises treatment of lignocellulose-containing materials with a solution containing phenol, whereby lignin can be made to dissolve and the cellulose and hemicellulose components set free.

10 Dual problems are associated with the management of solutions obtained in phenol digestion of lignocellulosic materials. It is required that the lignin in solution is recovered in a way which is the easiest possible and consumes little energy, while on the other hand the phenol in the solution must be recoverable and returnable to the process.

One way to circulate phenol and to recover lignin from the organic phase of phenol digestion is to distil the free phenol either at atmospheric or subatmospheric pressure and to solve the distillation residue in a suitable solvent, such as acetone or dioxane. This organic solution may be precipitated in an organic solvent, such as diethylether or toluene. The lignin which has thus been precipitated is then isolated by filtering or centrifuging, and it is washed with pure ether or toluene. This type of prior art is represented e.g. by Schweers et al., *Holzforschung* 26 (1972), 3, p.102. For several reasons, however, this precipitation procedure is difficult to apply on industrial scale. The first difficulty which may be mentioned is that at precipitation with the aid of an organic fluid part of the lignin remains in solution, that is, lignin fractioning occurs. This lignin fraction has turned out difficult to isolate, and it remains solved in the phenol residue. Secondly, handling large quantities of organic liquids on industrial scale is inconvenient and dangerous, and requires costly apparatus investments.

Another way to utilize the lignin in phenol digestion is to subject the lignin residue after distillation of the free phenol either to pyrolysis (cf. Schweers et al., *Das Papier* 26 (IUA), p. 585-590 (1972)) or to hydrocracking. The lignin will then decompose to various phenolic compounds. Attempts have been made to use these compounds together with the free phenol isolated from the digesting solution in fresh digesting solution management, which would make the process self-sufficient regarding make-up phenol. This however entails considerable difficulties in the digesting process itself because the properties of the pulps that are obtained are not constant and fluctuate in accordance with the changes in digesting solution composition. Moreover, pyrolysis as well as hydrocracking require very heavy plant apparatus, representing expensive investment and therefore impairing the economy of the entire phenol digestion process.

Phenol digestion processes of prior art have presented the serious drawback that washing with water has been employed in order to remove the spent digesting fluid from the cellulose fibres, and at this washing re-precipitation of already solved lignin on the cellulose fibres takes place. One has therefore introduced the use of a separate washing solution, such as an organic solvent or lye solution.

35 The object of the present invention is a procedure in which not only precipitation of lignin on cellulose fibre is prevented, but also circulation of the phenol used in the phenol digestion process, and in which no organic solvents need be used in the washing steps. The procedure of the invention for recirculating phenol in a lignocellulosic materials digestion process wherein lignocellulosic material is digested with phenol-containing solutions for solving the lignin is characterized in that recirculation of phenol is carried out in a cyclic process in which phenol-containing solution is first used in the washing step of the cellulose material coming from phenol digestion, thereafter in the lignocellulosic material digestion step, and finally in a lignocellulosic material impregnation step prior to the phenol digestion process.

45 The phenol digestion process is here understood to be a process in which lignocellulosic material, such as wood, straw, chaff, bark residues, leaves and other plant materials are heated in the presence of a phenol-containing solution, advantageously an aqueous solution, at elevated temperatures, e.g. at 90-110°C. Phenol is in this context understood to be not only hydroxybenzene but also other commercially available phenols and other phenol compounds, as well as phenolic compounds obtained by various methods from lignin. The phenol-containing solution advantageously contains hydrated acid, such as a mineral acid.

50 In the above-mentioned process lignin is solved in the phenol-containing digesting liquid. Separation of this spent digesting liquid by filtering and its reuse as digesting solution or as part thereof is known in the art. However, such reuse has the consequence that impurities and decomposition and polymerisation products of hemicelluloses and lignin are enriched in the solution and as a result solutions are obtained which are exceedingly difficult to manage.

55 In the procedure of the invention, both separation of lignin from the cellulose fibres after phenol digestion and returning the phenol in continuous manner to the process have been achieved in a particularly efficient way, without expensive recovery procedures such as are employed in prior art, e.g. distilling, pyrolysis and hydrocracking.

60 In the procedure of the invention a cyclic process is utilized in which one and the same phenol-containing solution circulates through certain steps in such manner that no detrimental accumulation of impurities takes place in the system. It is thus understood that one and the same solution is used and manipulated, first, in the washing steps of the cellulose material coming from phenol digestion, thereafter in the lignocellulosic material digestion process, and finally in a step in which the lignocellulosic material coming to be digested is

impregnated.

The cellulose material departing from phenol digestion contains the spent phenol-containing digesting liquid, which contains in solution lignin that was present in the lignocellulosic material. This spent digesting liquid is removed from the cellulose material by displacing it with regenerated phenol solution having high phenol content. The phenol concentration of this regenerated solution is advantageously in the range from 30 to 90% and its temperature is advantageously in the range from 40 to 90°C. Owing to the high phenol content and elevated temperature, the lignin remains in the displaced solution and is not precipitated back on the cellulose fibres. The cellulose material obtained in this way has substantially higher purity and is easier to wash than would be the case had the cellulose material in conventional manner been first washed with water.

The spent lignin-containing digesting solution displaced from the cellulose material is used, according to the invention, to impregnate the lignocellulosic material arriving at digestion. In the impregnation the water content of the lignocellulosic material and the diffusion of chemicals can be controlled. To this end, the temperature of the spent digesting liquid may be adjusted to be appropriate and, if desired, requisite chemicals may be added thereto. Impregnation also enhances the digestion process proper which is carried out henceforth.

After the displacement mentioned, the cellulose material contains regenerated phenol solution with high phenol content that was used in the displacement operation. As taught by the invention, in the next step a washing process is carried out, in which said regenerated phenol solution is removed, in its turn, by displacement. Advantageously a dual-step washing process is applied in which as its last phase displacement using pure water is performed. The solution displaced in the last washing step is used for displacement liquid in the first washing step to displace the regenerated phenol solution.

The displaced regenerated phenol solution now contains more water, owing to the washing water introduced in the system in the last washing step. This extra water can be removed in the procedure of the invention by lowering the temperature of the solution, whereby a phase with ample phenol content and an aqueous phase containing little phenol are formed. As taught by the invention, said phenol phase is used after the above-mentioned impregnation step to displace the impregnating liquid, whereby it serves, in other words, as digesting liquid for the lignocellulosic material. At this stage one may add to it the requisite make-up phenol and any other chemicals that may be required. The aqueous phase containing little phenol is utilized in the regeneration step in the procedure of the invention.

In the regeneration step the impregnating liquid displaced after the lignocellulosic material impregnating step is treated, this liquid consisting, as stated above, of the spent digesting liquid displaced from the cellulose material subsequent to the digestion step. As taught by the invention, this regeneration of the liquid is carried out by treating the liquid at elevated temperature with water or with a water-containing liquid, whereby two phases are produced. One is the organic phase containing lignin, which can be separated by decanting. The other phase is a phenol-containing aqueous phase, which is used to displace the digesting solution after phenol digestion. Any kind of water may be used in the treatment at elevated temperature, but it is advantageous to use the above-mentioned water-containing phase which was obtained by lowering the temperature of the phenol solution displaced in the first washing step and by separating the obtained aqueous phase with little phenol content, e.g. by decanting. A temperature between 30 and 80°C, advantageously between 40 and 60°C, may be applied in the regeneration.

It is thus understood that the procedure of the invention contains a cyclic process for recirculating phenol, in which only make-up chemicals are introduced in the system and lignin is removed in a continuous process.

The invention is described in the following, referring to the figure attached, which presents the process chart devised for implementing an embodiment of the invention. In the figure, the lignocellulosic material impregnation apparatus is indicated with reference numeral 10, the phenol digestion step with 20, the digesting solution displacing step with 30, the first and second cellulose material washing steps with 40 and 50, the decanting means with 60 and the phenol solution regenerating step with 70.

In the embodiment of the figure, the lignocellulosic material 11 is first treated with impregnating solution 33 in the impregnation step 10. The impregnating solution 33 consists of spent digesting liquid, as shall be stated later on. After impregnation, the impregnating liquid is removed from the impregnation step by displacing it with phenol-containing digesting solution 14. Reference numeral 21 indicates the lignocellulosic material flow impregnated with digesting solution, going to the digestion step 20.

From the digestion step 20 the cellulose material is conducted, in a flow indicated with 31, to the displacement step 30, where the spent digesting liquid is displaced with a displacement liquid 32. The cellulose material is thereafter conducted, in a flow indicated with 41, to the first washing step 40, where the liquid therein contained is displaced with liquid 42 coming from the second washing step 50. The cellulose material is thereafter conducted, in a flow indicated with 51, to the second washing step, where the liquid therein contained is displaced with water 52.

Disclosure of the essential features of the invention begins at the digestion step 20, whence the cellulose material that has been digested with phenol is conducted in a flow 31 to the displacement step 30. Here, the liquid is displaced from the cellulose with phenol solution 71,32 coming from the regeneration step 70. It is specific to this step that the phenol content of the displacing liquid is high and the temperature elevated. The lignin will then be efficiently washed out from the cellulose fibres and will not precipitate on the fibres.

Subsequent to displacement, the cellulose is conducted in a flow 41 to the first washing step 40, where the phenol-containing liquid is displaced with liquid that has been displaced in the second washing step 50, and which is indicated by reference numerals 53 and 42. The second washing step is similar to the first washing

step, except that the displacement liquid 52 is pure water in this instance. The washed cellulose flow departing from the second washing step 50 is indicated by reference numeral 54.

The phenol-containing liquid 43 that has been displaced in the first washing step 40 is next conducted to the decanting means 60, where the temperature of the liquid is lowered, e.g. with the aid of a heat exchanger not depicted. Two phases will then separate which can be separated from each other e.g. by decanting. One phase consists of an aqueous solution containing phenol in ample quantity, and which is conducted in a flow indicated with 62 and 14, to the impregnating step 10, where it displaces the impregnating liquid present in the lignocellulosic material. Reference numerals 12 and 13 indicate the facility for adding make-up phenol and additive chemicals.

The other phase separating in the decanting means 60 is an aqueous phase containing little phenol, and which is conducted in a flow indicated by 61, to the regeneration step 70. The temperature of the aqueous phase 61 may be raised, e.g. with a non-depicted heat exchanger, to the temperature required in regeneration.

In the regeneration step 70, from the spent digesting liquid 74 displaced in the impregnation step 10 the lignin therein contained is separated. Separation is effected at elevated temperature with the aid of the aqueous phase 61 coming from the decanting means 60. Two phases are hereby formed, one of them the organic phase 73 containing lignin and only little phenol, and the other an aqueous phase with ample phenol content, indicated with 71 and 32 and used to displace the spent digesting solution from the cellulose material 31 coming from the digestion step 20. The phenol-containing liquid 71,32 coming from the regeneration step 70 is already at a suitably high temperature, but its temperature may be controlled with the aid of a non-depicted heat exchanger, if required.

Example 1

In the example is demonstrated the significance of a separate impregnation step in view of delignification.

Birch wood chips were digested on laboratory scale. Table 1 presents the conditions that were applied, and the results obtained.

Table 1.

Management data and pulp state characteristics in birch digestions

No.	<u>Composition of digesting solution</u>				Liquid Digestion time, min.	Digestion temp., °C	Digestion Yield, Cl number %	
	Phenol, % b.w.	Water, % b.w.	HCl in the water, % b.w.	Wood				
R10	70	30	1.0	4:1	180	102	49.3	10.1
R11	70	30	1.0	4:1	90+90	102	46.3	6.1

In the test R11, the first 90 min. constituted the impregnation step, whereafter the impregnating solution was exchanged for fresh digesting solution. Compared with test R10, which had no separate impregnation step, the chlorine number was 4 units (40%) lower.

Example 2

It is demonstrated in the experiment how composition of washing solution and mode of washing affect the delignification.

Washing conditions

Test R4

1. 11% phenol
89% water
0.5% HCl (calc. on water)
 $V = 14 \text{ m}^3/\text{ts}$
 $T = 65-70^\circ\text{C}$
2. Water
 $V = 20 \text{ m}^3/\text{ts}$
 $T = 50^\circ\text{C}$

Test R10

1. Digesting solution expressed to consistency about 23%
2. 70% phenol
30% water
0.5% HCl (calc. on water)
 $V = 8 \text{ m}^3/\text{ts}$
 $T = 90^\circ\text{C}$
3. Water
 $V = 20 \text{ m}^3/\text{ts}$
 $T = 90^\circ\text{C}$

The conditions employed, and the results obtained, are shown in Table 2.

Table 2.

Management data and pulp state characteristics in birch digestion

<u>No. Composition of digesting solution</u>								
Phenol, Water, HCl Liquid Digestion Digestion Yield, C1 number								
	% b.w.	% b.w. in the	Wood	time,	temp.,	%		
		water,		min.	$^\circ\text{C}$			
		% b.w.						
R10	70	30	1.0	4:1	180	102	49.3	10.1
R4	70	30	1.0	4:1	180	102	62.1	24.8

By using the fresh digesting solution for initial washing liquid and efficiently removing the spent digesting solution, lignin is prevented from precipitating back on the fibres, whereby the C1 number is about 15 units (60%) lower.

Example 3

In the example is demonstrated how the washing event affects delignification.

Washing conditions

Test R5

1. 70% phenol
30% water
0.5% HCl (calc. on water)
 $V = 8 \text{ m}^3/\text{ts}$
 $T = 80^\circ\text{C}$
2. Water
 $V = 20 \text{ m}^3/\text{ts}$
 $T = 90^\circ\text{C}$

Test R10

1., 2. as in the preceding, but digesting solution expressed before washing.

Table 3 shows the conditions employed and the results obtained.

Table 3.

Management data and pulp state characteristics in birch digestions

No.	<u>Composition of digesting solution</u>							
	Phenol, % b.w.	Water, % b.w.	HCl in the water, % b.w.	Liquid :Wood	Digestion time, min.	Digestion temp., °C	Yield, %	Cl number
R5	70	30	1.0	4:1	180	102	50.6	14.2
R10	70	30	1.0	4:1	180	102	49.3	10.1

By efficiently removing spent digesting solution at the beginning of the digestion step the chlorine number is brought down 4 units (29%).

Claims

1. A process for recirculating phenol in a lignocellulosic materials digestion process in which lignocellulosic material is digested with phenol-containing solutions in order to dissolve lignin, characterised in that phenol recirculation is carried out as a cyclic process in which the phenol-containing solution is first used in the washing of the cellulosic material from the phenol digestion, thereafter in the lignocellulosic material digestion step, and finally in a lignocellulosic material impregnation step preceding the phenol digestion process.

2. A process as claimed in Claim 1 characterised in that in the washing of the cellulosic material from the phenol digestion the spent digesting liquid is displaced with a regenerated phenol solution of high phenol content, and that the displaced digesting liquid is used in the lignocellulosic material impregnating step preceding the phenol digestion process.

3. A process as claimed in claim 2 characterised in that after displacement of the digesting liquid the cellulose material is washed in two steps, in the first washing step the regenerated phenol solution being displaced with washing liquid that has been displaced in the second washing step with the aid of water.

4. A process as claimed in claim 3 characterised in that the temperature of the phenol-containing solution displaced in the first washing step is reduced so that a phenol-rich phase and a water-containing phase are formed, whereafter the phenol-rich phase is used to displace the impregnating solution from the lignocellulosic material and to digest the lignocellulosic material, and the water-containing phase is led to the regeneration step.

5. A process as claimed in claim 4 characterised in that desired additive chemicals are added to the phenol-rich phase prior to displacing the impregnating solution.

6. A process as claimed in claim 4 characterised in that in the regeneration step the lignin-containing solution displaced after the lignocellulosic material impregnation step is treated with water at elevated temperature, so as to give a lignin-containing phase and a phenol-containing aqueous phase, the latter being used to displace the digesting solution after the phenol digestion.

7. A process as claimed in claim 6 characterised in that in the regeneration step the treatment at elevated temperature of the lignin-containing solution is carried out using said water-containing phase, which, if required, has been heated to the elevated temperature used in regeneration.

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