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(54) KRAFT COOKING METHOD USING POLYSULFIDE COOKING LIQUOR

KRAFT-KOCHVERFAHREN MIT EINER POLYSULFIDKOCHLAUGE

PROCÉDÉ DE CUISSON KRAFT UTILISANT UNE LIQUEUR DE CUISSON AU POLYSULFURE

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method for the preparation of kraft pulp with increased pulping yield from lignin-containing cellulosic material using polysulfide cooking liquor.

BACKGROUND OF THE INVENTION

[0002] In conventional kraft cooking implemented in the 1960-1970-ies in continuous digesters was the total charge of white liquor added to the top of the digester. It soon emerged that the high alkali concentrations established at high cooking temperatures was detrimental for pulp viscosity.

[0003] Cooking methods was therefore developed in order to reduce the detrimental high alkali peak concentrations at start of the cook, and thus was split charges of alkali during the cook implemented in cooking methods such as *MCC, EMCC, ITC* and *Lo-Solids* cooking.

[0004] Other cooking methods was implemented using black liquor impregnation ahead of cooking stages where residual alkali in the black liquor was used to neutralize the wood acidity and to impregnate the chips with sulfide. One such cooking method sold by Metso is *Compact Cooking* where black liquor with relatively high residual alkali level is withdrawn from earlier phases of the cook and charged to a preceding impregnation stage.

[0005] One aspect of alkali consumption during the cooking process, i.e. including impregnation, is that a large part of the alkali consumption is due to the initial neutralization of the wood acidity, and as much as 50-75% of the total alkali consumption is occurring during the neutralization process. Hence, a lot of alkali is needed to be charged to the initial neutralization. This establish a cumbersome problem as high alkali concentrations had been found to be detrimental for pulp viscosity when charged to top of digesters in conventional cooking. One solution to meet the high alkali consumption and necessity to reduce alkali concentration in top of digester was to charge large volumes of alkali treatment liquors, preferably black liquor having a residual alkali content, but having low alkali concentration, which resulted in presence of relatively large amount of total alkali per kg of wood material but still at low alkali concentration.

[0006] IN US7270725 (=EP1458927) Metso disclosed a pretreatment stage using polysulfide cooking liquor ahead of black liquor treatment. In this process was the polysulfide treatment liquor drained after the pretreatment stage and before starting the black liquor treatment. The polysulfide treatment stage was also preferably kept short with treatment time in the range 2-10 minutes.

[0007] In a recent granted US patent, US7828930, is shown an example of a kraft cooking process where 100% of the cooking liquor, in form of polysulfide liquor also named as orange liquor, is charged to top of digester and start of an impregnation stage. Here is also the temperature raised from 60°C to 120°C at start of the polysulfide treatment stage. However, as shown in example 1 is a liquor to wood ratio of about 3.5 established in the top of the digester by adding a proper amount of water. This order of liquor/wood ratio is often perceived as a standard liquor/wood ratio in continuous cooking necessary for a steady process. According to this proposal is a part of the residual polysulfide treatment liquor at relative high alkali concentration withdrawn and replaced with cooking liquor at relative low alkali concentration at start of the cooking stage, and the withdrawn residual polysulfide treatment liquor is added at later stages of the cook.

[0008] There has thus been an ongoing development of cooking methods where both alkali concentrations at start of cook is reduced, and increased yield from the cooking process is sought for using among others addition of polysulfide cooking liquor that stabilize the carbohydrates.

[0009] US 3664919 A discloses a method for impregnating lignocellulosic material, previously saturated with water, in a first stage with an alkaline polysulphide cooking liquor, removing excess liquor, and then cooking the impregnated material in a second stage by rapidly heating with steam.

[0010] C A2763651 A1 discloses a continuous digestion method using a digester equipped inside with a top zone, an upper digestion zone, a lower digestion zone, and a digestion/cleaning zone which have been arranged in this order from the top toward the bottom, each zone having a strainer disposed at the bottom, and a black liquor extracted through at least one of the strainers being discharged from the digestion system.

[0011] US 3567572 A discloses a process for the production of cellulosic pulp from lignocellulosic materials which comprises substantially completely impregnating said materials in subdivided form with a polysulphide liquor containing no added sodium hydroxide at a temperature below that at which substantial decomposition of the polysulphide occurs, removing excess polysulphide liquor from the impregnated materials, stabilizing the impregnated materials against alkaline degradation by increasing the temperature of said materials and subsequently delignifying said stabilized materials by cooking said material in a cooking liquor containing sodium hydroxide.

[0012] US 2009/126883 A1 discloses a method for Kraft pulping, wherein the total required alkali charge is added to the beginning of a cook, and after all polysulfide has essentially reacted with lignocellulosic material at temperature below that at which no significant carbohydrate degradation occurs, a first quantity of the cooking liquor high in effective alkali concentration is removed from a first point in the pulping process and replaced with a cooking liquor low in effective alkali concentration removed from another process point.

[0013] WO 99/14423 A1 discloses a process for producing pulp from cellulosic fiber, wherein the cellulosic fiber material is impregnated with polysulfide before cooking followed by extraction of spent cooking liquor. A portion of the spent cooking liquor is gasified to hydrogen sulphide and treated to form an acidic gas comprising hydrogen sulphide and carbon dioxide.

[0014] WO 03/057979 A1 discloses a method for the manufacture of cooked cellulose pulp in which the starting material undergoes a successive increase in temperature towards cooking temperature while the chips are first treated in a pretreatment zone in which the main part, greater than 50%, of fresh white liquor necessary for the cooking stage is added, after which this alkali-rich treatment fluid is withdrawn and replaced to a major extent by black liquor.

SUMMARY OF THE INVENTION

[0015] The present invention is provided by the appended claim 1. Beneficial embodiments are provided in the dependent claims. Accordingly, the invention is based upon the surprising finding that concentration of polysulfide should be kept high in a low temperature pretreatment stage at relatively long retention time before cooking, using liquor to wood ratios well below that as commonly used. The stabilization effect of carbohydrates, the major objective for polysulfide addition, has shown to be improved dramatically if using a liquor to wood ratio of about 2,9 instead of the conventional liquor to wood ratio of about 3,5, and all other conditions equal. This non proportional effect of low liquor to wood ratio has not been disclosed or realized before despite the numerous proposals for improving cooking yield using polysulfide cooking liquor.

[0016] One object of the present invention is to provide an improved method for the preparation of kraft pulp with increased pulping yield from lignin-containing cellulosic material using polysulfide cooking liquor, wherein the lignin-containing cellulosic material is heated to a temperature in the range 50-100 °C followed by adding polysulfide cooking liquor to a first impregnation stage which in turn is followed by cooking stages resulting in a kraft pulp with a kappa number below 40, and wherein the impregnation stage is conducted at high alkali concentration, low temperature and high polysulfide concentration using polysulfide cooking liquor at a liquor-to-wood ratio in the range 2.0 to 3.2 , and that the temperature is between 80-120°C during a retention time resulting in a H-factor in the range 2-20 and preferably 2-10 of the impregnation stage. This low H-factor is indicative for that no cooking or delignification effect is obtained in the first impregnation stage, and hence is no reduction in pulp viscosity seen as could be the case if high alkali concentrations are at hand in cooking stages at higher temperatures.

[0017] According to the present invention the effective alkali concentration during the impregnation stage is above 60 g/l when adding the polysulfide cooking liquor.

[0018] According to the present invention the polysulfide concentration during the impregnation stage is above 3 g/l, or above 0,09 mol/l, when adding the polysulfide cooking liquor.

[0019] According to the present invention more than 90% of the total charge of cooking liquor needed for completion of the cooking stages to the intended kappa number below 40 is charged to the first impregnation stage, and that at least 175 kg of alkali (EA as NaOH) per ton of chips is charged for softwood and at least 160 kg of alkali per ton of chips for hardwood.

[0020] According to the present invention is the alkali concentration reduced by at least 8 g/l by adding additional cooking liquids having less alkali concentration than the alkali concentration prevailing at end of the first impregnation stage when increasing the temperature to cooking temperature, said cooking liquids in at least part thereof includes black liquor.

[0021] In a preferred embodiment of the method is no black liquor added to the first impregnation stage.

[0022] When using the inventive method has also preferably the white liquor added to the first impregnation stage an alkali concentration above 100 g/l and a polysulfide concentration above 4 g/l.

[0023] The lignin-containing cellulosic materials to be used in the present process are suitably softwood, hardwood, or annual plants.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024]

FIG. 1 is a schematic cooking system capable of implementing the inventive method;

FIG. 2 demonstrate an example of the alkali profile established with the inventive method;

FIG. 3 show the dramatic impact on increased yield when increasing the polysulfide concentration above 0.15 mol/L

FIG. 4 show the relative stabilization of carbohydrates as a function of liquid to wood ratio during the impregnation stage.

DETAILED DESCRIPTION OF THE INVENTION

[0025] In figure 1 is shown a 2-vessel kraft cooking system, having a first hydraulic impregnation vessel B and a second steam/liquid phase digester C, wherein the inventive method could be implemented. In this type of system is first the lignin containing cellulosic material Ch fed to a bin A wherein the cellulosic material is heated to a temperature in the range 50-100 °C by using addition of steam St. The lignin containing cellulosic material could preferably be wood chips. From the lower part of the bin A is then the heated chips suspended in treatment liquor in a chute C located above the high pressure sluice feeder SF. The treatment liquor here is preferably only polysulfide cooking liquor, WL, and preferably is the entire charge of cooking liquor needed for the cooking process charged here.

[0026] The chips suspended in the treatment liquor are fed to the sluice feeder and displaced liquid is fed out from the bottom outlet of the sluice feeder and returned to the chute in a low pressure circulation. The chips in the sluice feeder is pressurized by the return flow from the vessel B and fed out to the top separator TS in top of the vessel B.

[0027] Thus, the first impregnation stage is implemented in the vessel B and preferably only with the polysulfide cooking liquor and as small amount as possible of additional liquids such as wood moisture, steam condensates, and especially no black liquor nor additional water or filtrates. The resulting liquor-to-wood ratio established should be in the range 2.0 to 3.2 and the temperature should be in the range 80-120°C.

[0028] After the sufficient retention time in vessel B, which should have a retention time resulting in an H-factor in the range 2-20 of the impregnation stage, the impregnated chips will be fed to the steam/liquid phase digester C together with the residual treatment liquor. Here is shown a conventional transfer system with dilution in bottom of the vessel B using withdrawn treatment liquor from the top separator TS in the top of vessel C. At this point is the chip suspension heated to full cooking temperature, in the range 140-170°C depending upon type of cellulosic material, and additional liquid is added in order to reduce the alkali concentration at this point. In this embodiment is shown addition of black liquor obtained from a screen section withdrawing black liquor and sending a part of this black liquor to recovery REC. Hence, no detrimental effects upon pulp viscosity would occur by this dilution with black liquor. In this embodiment is shown a digester C with 2 concurrent cooking zones, one cooking zone above the first screen section and a second cooking zone above the final screen section in bottom of digester. In a conventional manner is a final counter current wash zone implemented in bottom of digester by addition of wash water/Wash. The final pulp with a kappa number below 40 is fed out from bottom in flow Pu.

[0029] In figure 2 is disclosed the alkali concentration profile that could be established in a system like that disclosed in figure 1, with alkali consumption of about 110 kg/BDT in the impregnation vessel, 45 kg/BDT in the first cooking zone in vessel C and 15 kg/BDT in last cooking zone in vessel C. In the top of the first impregnation vessel B is an alkali concentration of about 67 g/l established and this alkali level drops down to about 32 g/l in the bottom of vessel B, where a dilution is made by return flows added to bottom. Combined with the dilution with black liquor in top of digester vessel C the cooking in top of digester starts at an alkali concentration of about 22 g/l. Due to the dilution to a liquor to wood ratio of about 6,5 is however sufficient total amount of alkali present. During the cook the alkali concentration drops evenly, first to a level of about 16 g/l at first withdrawal screen, and finally down to about 8 g/l in final withdrawal screen. It is to be noted that a part of the withdrawn black liquor at concentration of about 16 g/l is recirculated back to top of vessel C. With this alkali profile is an improved usage of the polysulfide obtained as it is used in the first impregnation stage at high alkali concentration, low temperature and high polysulfide concentration.

[0030] In figure 3 is disclosed the improved carbohydrate yield as a function of the polysulfide concentration, when about 1% lignin is still present in the pulp. Here is shown the dramatic increase in yield when increasing the polysulfide concentration above 0,15 mol/L. There is basically a linearly increasing yield when the concentration increases between 0 to 0,15 mol/l. In this initial range is the yield increased from about 45% up to about 46.2%. However, when the concentration reach 0,2 mol/L is the yield increased to about 48,3%.

EXAMPLES

[0031] A series of tests has been made simulating a system as that shown in figure 1 using a white liquor having an alkali concentration of about 117 g/L and a polysulfide concentration of about 6 g/l. The charges of flows to the first impregnation stage are in tests #1-7 using part flows a-e. This results in a liquor to wood ratio shown in row L/W. The respective concentrations established are shown in rows f to j. S_nS^{2-} Despite the presence of a number of different polysulfide ions, each polysulfide ion can be considered to consist of one atom "sulfide sulfur", i.e. sulfur in the formal oxidation state S(-II), and n atoms of polysulfide "excess sulfur", i.e. sulfur in the formal oxidation state S(0).

$$[S\text{-}II)]=[HS^-]+\sum[S_nS^{2-}]$$

$$[S(0)]=\sum n[S_nS^{2-}]$$

[0032] Finally, the Xs factor has been calculated using the formula:

$$Xs = [S(0)] / [S(-II)]$$

and the carbohydrate stabilization has been calculated using the formula*:

$$\mathrm{Log}\,[S(0)] + 1.7\log[OH^-] - 1.6\log(1/Xs - 1/4)$$

(*see Teder, A. (1965):Svensk Papperstidn. 68:23, 825)

		#1	#2	#3	#4	#5	#6	#7
a	WL (m^3/BDT)	1,79	1,79	1,79	1,79	1,79	1,79	1,79
b	Moisture (m^3/BDT)	0,82	0,82	0,82	0,82	0,82	0,82	0,82
c	Condensate (m^3/BDT)	0	0,3	0,3	0,3	0,3	0,3	0,3
d	BL to feed (m^3/BDT)	0,0	0,0	0,0	0,5	1,0	1,5	2,0
e	Knots to feed (m^3/BDT)	0	0	0,3	0,3	0,3	0,3	0,3
	L/W	2,61	2,91	3,21	3,71	4,21	4,71	5,21
f	NaOH (g/L)	80,4	72,1	65,9	59,2	54,1	50,0	46,8
g	OH (mol/L)	2,0	1,8	1,6	1,5	1,4	1,3	1,2
h	PS (g/L)	4,12	3,70	3,35	2,90	2,56	2,28	2,07
i	PS (mol/L)	0,13	0,12	0,10	0,09	0,08	0,07	0,06
j	HS (mol/L)	0,07	0,08	0,10	0,11	0,12	0,13	0,14
	Xs	1,81	1,37	1,1	0.83	0,67	0,56	0,48
	Carbohydrate stab (test #3 is reference)	220	134	100	68	47	31	19

[0033] In figure 4 is disclosed the relative carbohydrate stabilization from above examples as a function of liquor to wood ratio during impregnation. The test #3 is used as the reference, i.e. 100%. The relative carbohydrate stabilization is roughly increasing linearly when decreasing the liquor to wood ratio during impregnation from 5,2 down to 3,7. However a dramatic improvement is obtained if the liquor to wood ratio is reduced to and further below 3,2. While the relative carbohydrate stabilization increase from about 19 to about 68 in the liquor to wood ratio from 5,2 down to 3,7, it is increased to astonishing 100 and further to about 134 and up to 220 at liquor to wood ratio of 3,2 , 2,9 and 2,6 respectively.

Claims

1. A method for the preparation of kraft pulp with increased pulping yield from lignin-containing cellulosic material using polysulfide cooking liquor, wherein the lignin-containing cellulosic material is heated to a temperature in the range 50-100 °C followed by adding polysulfide cooking liquor to a first impregnation stage which in turn is followed by cooking stages resulting in a kraft pulp with a kappa number below 40 **characterized in that** the impregnation stage

is conducted at high effective alkali concentration above 60 g/l when adding the polysulfide cooking liquor, low temperature and high polysulfide concentration above 3 g/l, or above 0,09 mol/l, when adding the polysulfide cooking liquor, using polysulfide cooking liquor at a liquor-to-wood ratio in the range 2.0 to 3.2, and that the temperature is between 80-120°C during a retention time resulting in a H-factor in the range 2-20 and preferably 2-10 of the impregnation stage,
wherein more than 90% of the total charge of cooking liquor needed for completion of the cooking stages to the intended kappa number below 40 is charged to the first impregnation stage, and that at least 175 kg of effective alkali (EA as NaOH) for softwood and 160 kg of effective alkali for hardwood per ton of chips is charged, and
wherein the alkali concentration is reduced by at least 8 g/l by adding additional cooking liquids having lower alkali concentration than the alkali concentration prevailing at end of the first impregnation stage when increasing the temperature to cooking temperature, said cooking liquids in at least part thereof includes black liquor.

2. The method according to claim 1, wherein no black liquor is added to the first impregnation stage.

3. The method according to claim 2, wherein the polysulfide cooking liquor added to the first impregnation stage has an alkali concentration above 100 g/l and a polysulfide concentration above 4 g/l .

Patentansprüche

1. Verfahren zur Gewinnung eines Kraftzellstoffs mit erhöhter Zellstoffausbeute aus Lignin enthaltenden Cellulosematerial unter Verwendung einer Polysulfid-Kochlauge, wobei das Lignin enthaltenden Cellulosematerial auf eine Temperatur in dem Bereich von 50-100°C erhitzt wird, gefolgt vom Hinzufügen von Polysulfid-Kochlauge zu einer ersten Imprägnationsstufe, die wiederrum gefolgt ist von Kochstufen, was in einem Kraftzellstoff resultiert, der eine Kappa-Zahl von unter 40 aufweist, **dadurch gekennzeichnet, dass**
die Imprägnationsstufe mit einer hohen effektiven Alkalikonzentration von über 60 g/l durchgeführt wird, wenn die Polysulfid-Kochlauge hinzugefügt wird, geringer Temperatur und hoher Polysulfid-Konzentration über 3g/l oder 0,09 mol/l, wenn die Polysulfid-Kochlauge hinzugefügt wird, unter Verwendung von Polysulfid-Kochlauge bei einem Laugezu-Holz-Verhältnis in dem Bereich 2,0 bis 3,2, und dass die Temperatur während einer Verweilzeit zwischen 80-120°C liegt, was in einem H-Faktor in dem Bereich von 2-20, bevorzugt 2-10 der Imprägnationsstufe resultiert,
wobei mehr als 90% der Gesamtladung der Kochlauge, die zum Abschluss der Kochstufen zu der angestrebten Kappa-Zahl von unter 40 benötigt wird, in der ersten Imprägnationsstufe hinzugegeben wird, und dass wenigstens 175 Kg von effektivem Alkali (EA als NaOH) für Weichholz und 160 Kg von effektivem Alkali für Hartholz pro Tonne Chips hinzugegeben werden, und
wobei die Alkalikonzentration um wenigstens 8 g/l reduziert wird durch Hinzufügen zusätzlicher Kochlaugen mit geringerer Alkalikonzentration als die Alkalikonzentration, die am Ende der ersten Imprägnationsstufe vorherrscht, wenn die Temperatur auf Kochtemperatur erhöht wird, wobei die Kochlaugen wenigstens in Teilen davon Schwarzlauge enthalten.

2. Verfahren gemäß Anspruch 1, wobei zu der ersten Imprägnationsstufe keine Schwarzlauge hinzugefügt wird.

3. Verfahren gemäß Anspruch 2, wobei die Polysulfid-Kochlauge, die zu der ersten Imprägnationsstufe hinzugefügt wird, eine Alkalikonzentration von über 100 g/l und eine Polysulfid-Konzentration von über 4 g/l aufweist.

Revendications

1. Procédé de préparation de pâte à papier kraft avec un rendement de mise en pâte accru à partir d'un matériau cellulosique contenant de la lignine en utilisant une liqueur de cuisson au polysulfure, dans lequel le matériau cellulosique contenant de la lignine est chauffé à une température dans la gamme allant de 50 à 100 °C suivi par l'addition de la liqueur de cuisson au polysulfure lors d'une première étape d'imprégnation qui ensuite est suivie de phases de cuisson résultant en une pâte à papier kraft avec un nombre kappa inférieur à 40
caractérisé en ce que l'étape d'imprégnation est effectuée à une concentration efficace élevée en base supérieur à 60 g/l lors de l'ajout de la liqueur de cuisson au polysulfure, à une basse température et à une concentration élevée en polysulfure supérieure à 3 g/1, ou supérieure à 0,09 mol/1, lors de l'ajout de la liqueur de cuisson au polysulfure, en utilisant la liqueur de cuisson au polysulfure selon un rapport liqueur-bois compris dans la gamme allant de 2,0 à 3,2, et **en ce que** la température est comprise entre 80 et 120 °C pendant un temps de rétention résultant en un facteur-H compris dans la gamme allant de 2 à 20 et de préférence allant de 2 à 10 de l'étape

d’imprégnation,
dans lequel plus de 90 % de la charge totale de la liqueur de cuisson nécessaire à la réalisation des étapes de cuisson au nombre kappa prévu inférieur à 40 est chargé lors de la première étape d’imprégnation, et qu’au moins 175 kg de base efficace (AE tel que NaOH) pour le bois tendre et 160 kg de base efficace pour le bois dur par tonne de copeaux sont chargés, et
dans lequel la concentration en base est réduite d’au moins 8 g/l par l’ajout de liquides de cuisson supplémentaires possédant des concentrations en base inférieures à la concentration en base prévalant à la fin de la première étape d’imprégnation lorsque la température augmente à une température de cuisson, lesdits liquides de cuisson dans au moins une partie de ceux-ci comprennent de la liqueur noire.

2. Procédé selon la revendication 1, dans lequel aucune liqueur noire n’est ajoutée lors de la première étape d’imprégnation.

3. Processus selon la revendication 2, dans lequel la liqueur de cuisson au polysulfure ajoutée lors de la première étape d’imprégnation possède une concentration en base supérieure à 100 g/l et une concentration en polysulfure supérieure à 4 g/1.

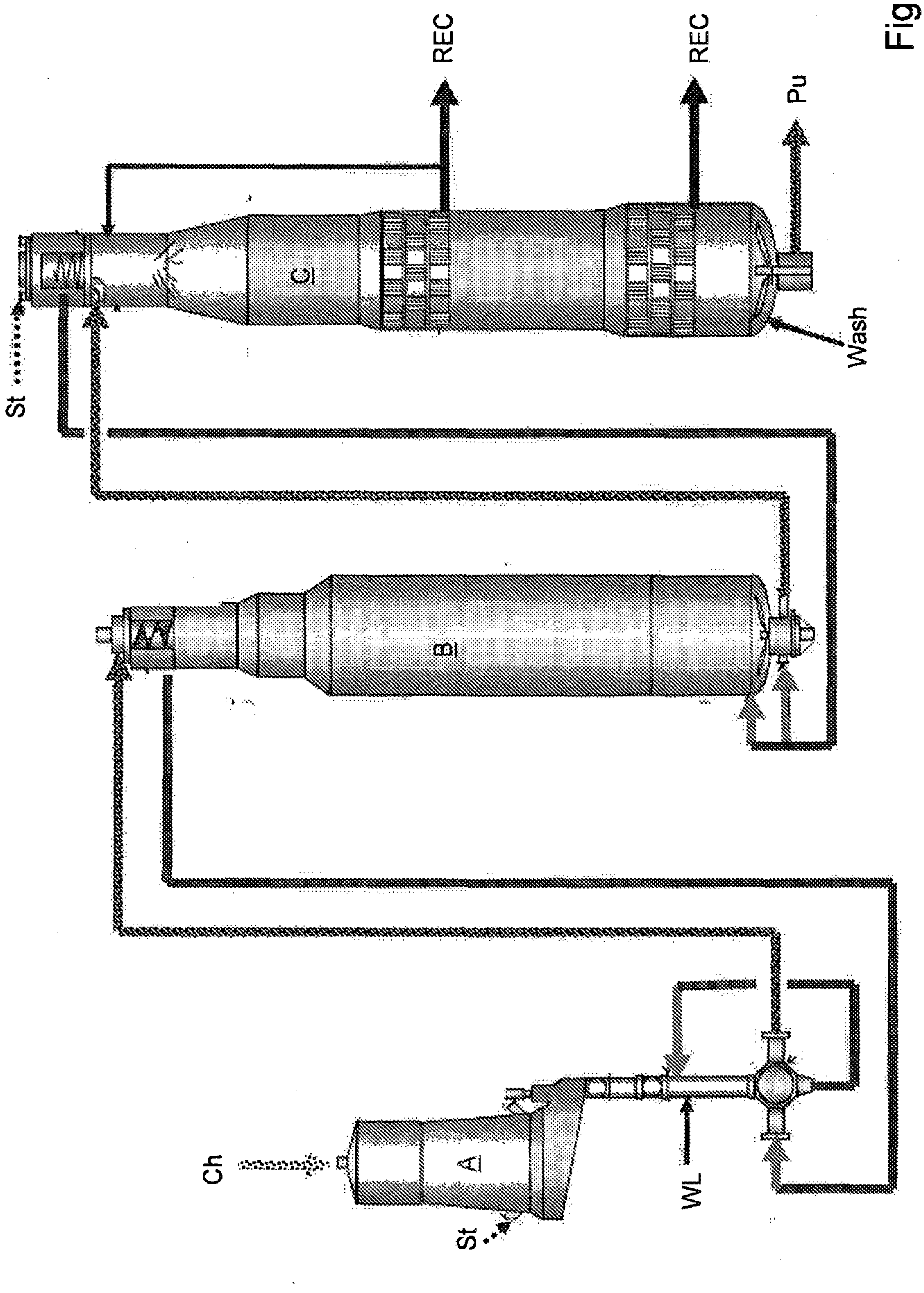


Fig. 1

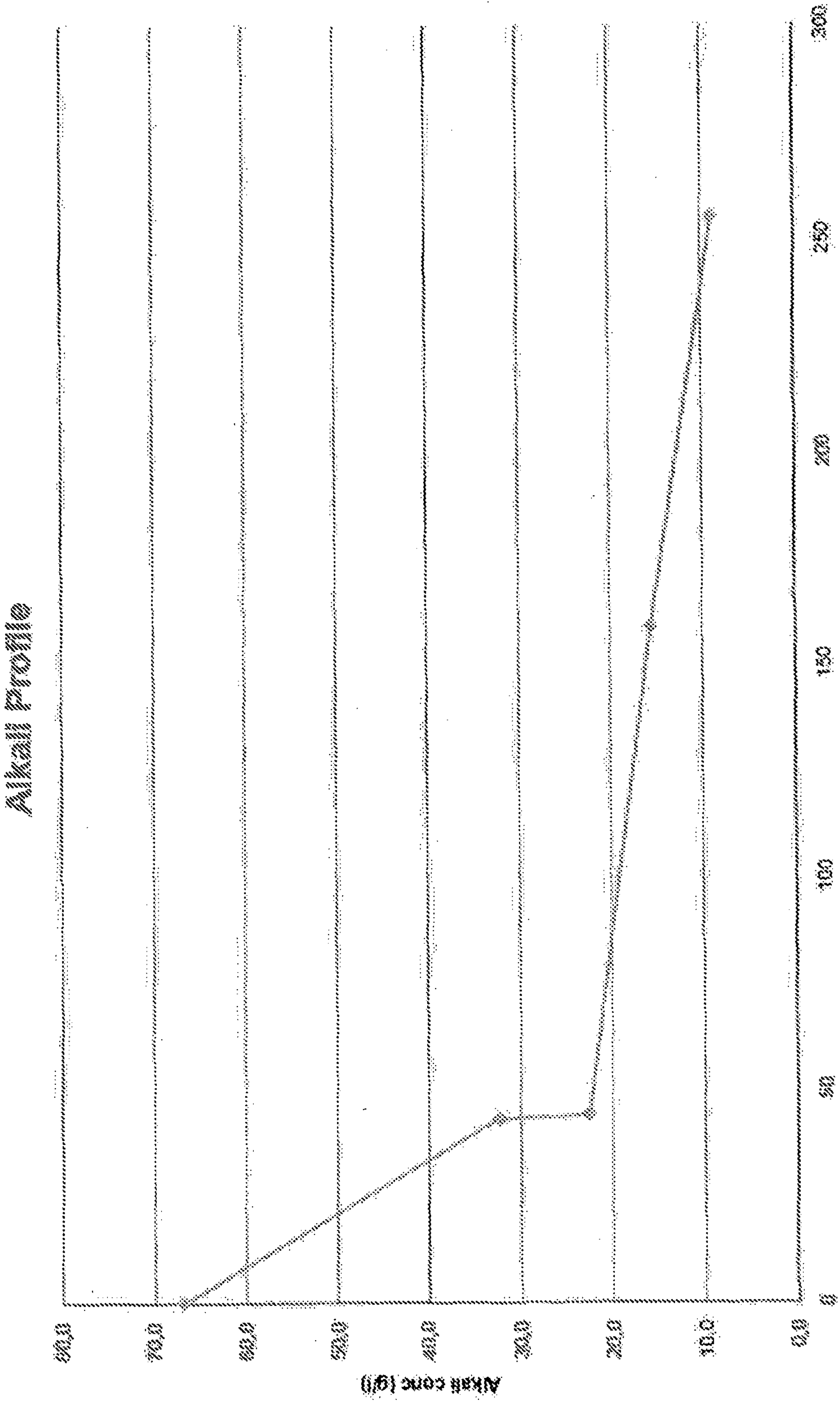
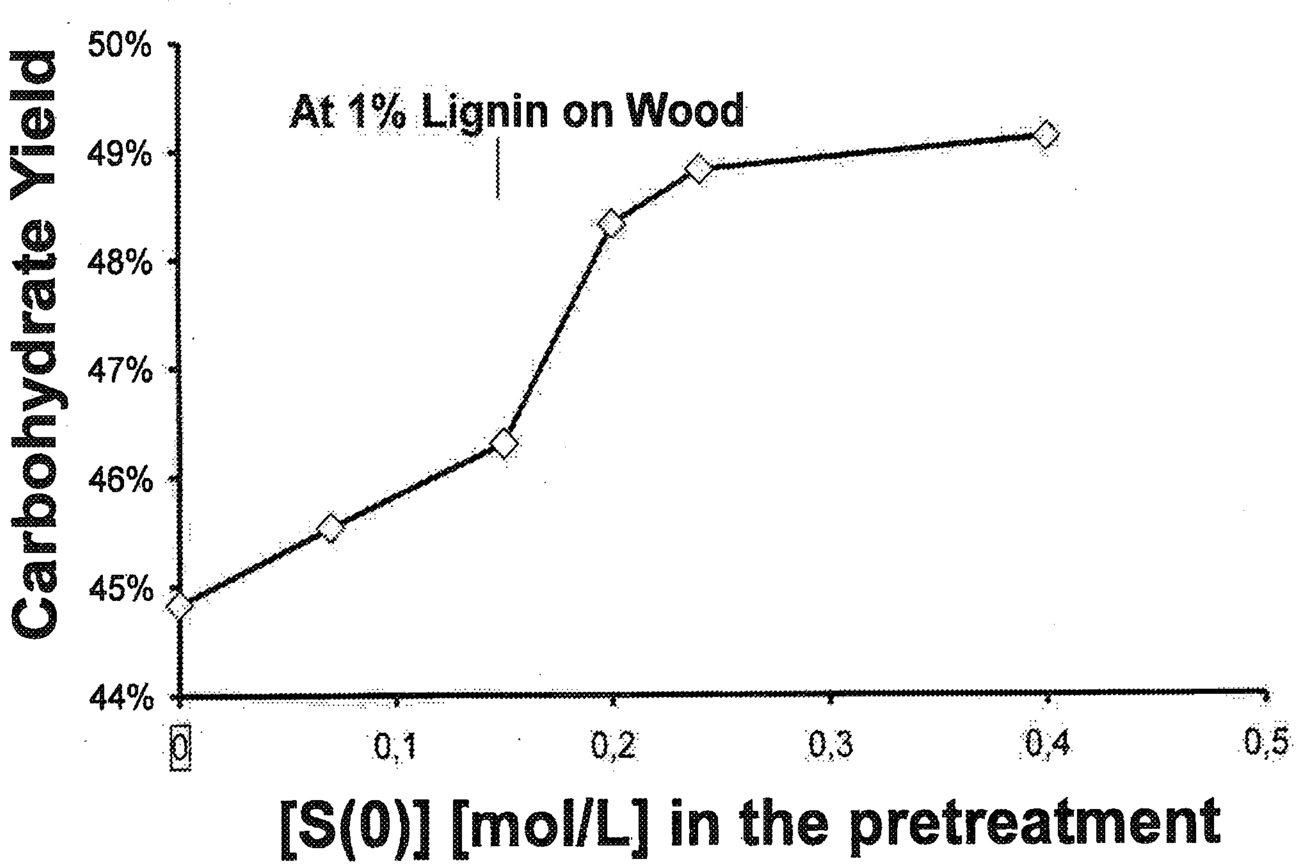

Alkali Profile
Alkali conc (g/l)
80,0
70,0
60,0
50,0
40,0
30,0
20,0
10,0
0,0
Retention time
0
50
100
150
200
250
300

Fig. 2

Fig. 3


Carbohydrate Yield
50%
49%
48%
47%
46%
45%
44%
At 1% Lignin on Wood
0
0,1
0,2
0,3
0,4
0,5
[S(0)] [mol/L] in the pretreatment

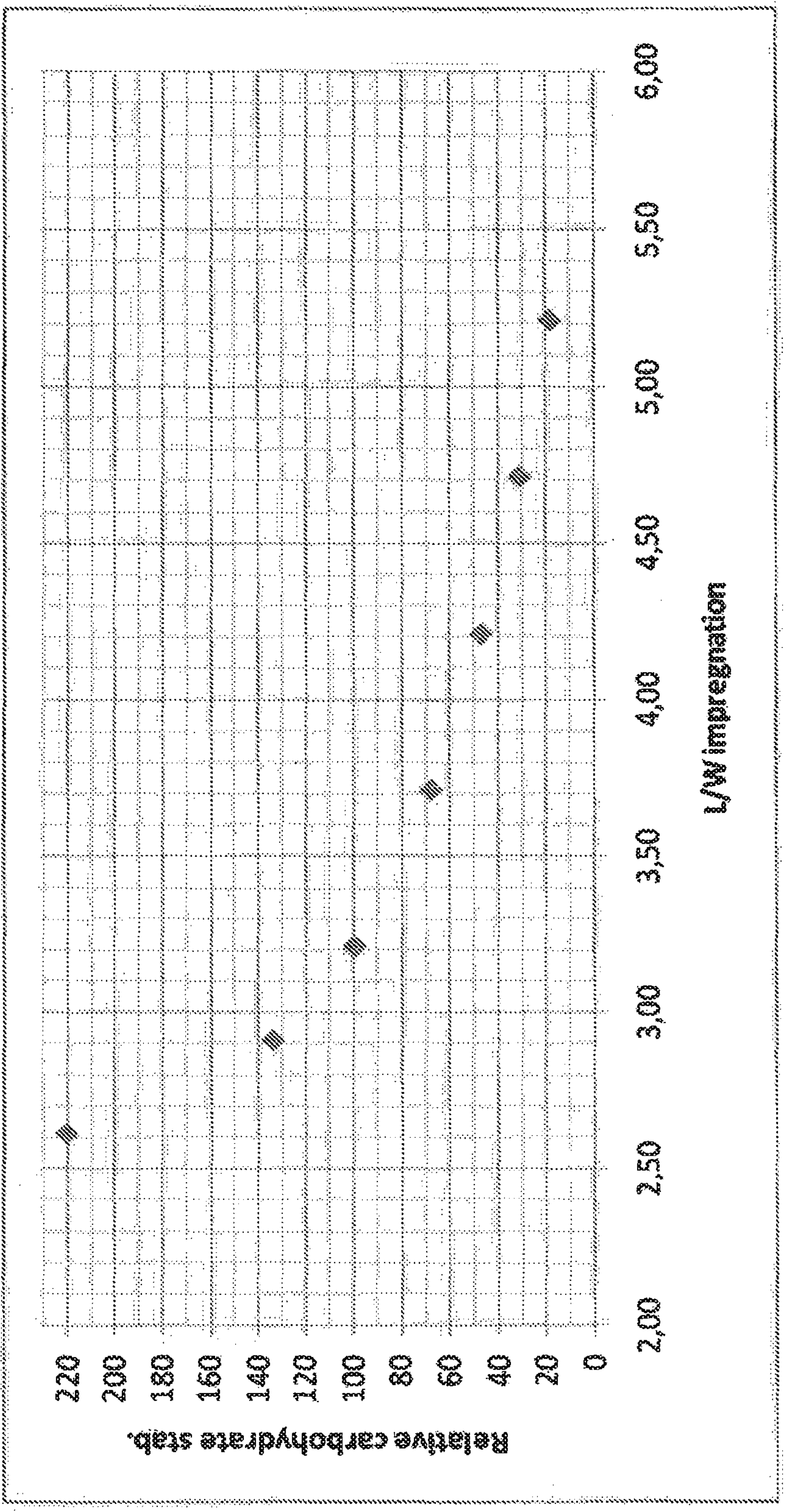

Relative carbohydrate stab.
220
200
180
160
140
120
100
80
60
40
20
0
2,00
2,50
3,00
3,50
4,00
4,50
5,00
5,50
6,00
L/W impregnation

Fig. 4

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