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(54) Explosion process for preparing pulp for paper making.

(57) This invention relates to an improved process preparing pulp suitable for papermaking, consisting of short time saturated steam cooking of chips impregnated with alkaline solutions of sulphites in the temperature range of 180 to 210° C, instantaneous pressurizing the reactor with cool nitrogen after cooking to a super atmospheric pressure of from 25 to 50 atm followed by explosive decompression and fibre refining.

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This invention relates to processes for the preparation of pulp for paper manufacture. More particularly, it relates to such processes which involve explosive decompression of wood fragments in the preparation of pulp.

Ingruber et al., Pulp and Paper Manufacture, Volume 4, TAPPI, CPPA, p.160 (1985) define that conventional ultra-high-yield chemithermomechanical (CTMP) or chemimechanical (CMP) pulping is preferably conducted at a pH level between 4 and 9, and involves either liquid or vapor phase cooking with sodium sulphite-bisulphite solutions for about 10 to 30 minutes at a temperature between 60 and 175 ° C. It is generally accepted that the chemical treatment is mainly responsible for permanent fibre softening, increase in long fibre content, fibre specific surface and conformability, as demonstrated by Heitner et al., Pulp and Paper Can., (84)11: T252-T257 (1983).

There is another softening approach which consists of a steam treatment of chips at high temperatures followed by explosive decompression.

The production of pulp using high-pressure and high-temperature steam chip softening well above glass transition temperatures of lignin should theoretically lead to lower energy consumption in subsequent refining stages.

The initial research in the field of high-pressure steam cooking, followed by defibration by explosion, was made by Mason, US-A-1 824 221; 2 645 623; 2 494 545; 2 379 8290. The masonite pulp obtained according to a two stage Sprout-Waldron refining procedure showed weak physical strength, dark colour and yield loss of 16% to 20%, and revealed itself simply unsuitable for the production of paper according to Koran et al., Pulp and Paper Can., 79(3): T107-T113 (1978). Mamers et al., TAPPI, 64(7): 93-96 (1981); APPITA, 29(5): 356-362 (1976) investigated explosion pulping of pinus elliotti wood chips with the help of high pressure carbon dioxide solutions, and bagasse of wheat straw explosion pulping under high pressure nitrogen. Paper properties which were obtained were similar to those of CTMP/CMP pulps, but at the expense of brightness. The major problems to overcome are oxidation, as well as hydrolytic degradation of fibres leading to brightness and yield loss.

It has been suggested by Vit and Kokta, Vit et al., CA-A-1 212 505 (1986) that the ultra-high-yield (90% +) pulp suitable for papermaking can be produced by vapor phase steam explosion cooking. The initial properties of papers made from exploded softwood chips were similar to those of thermomechanical pulping (TMP). However, refining energy was about 20% to 25% lower. Recently, a pulping process entitled "Process for Preparing Pulp for Paper Making", Kokta B.V., CA-A-1 230 208 (1987); US-A- 4 798 651 (1989); Can. Pat. Appl. No. 542 643 (May 1987), referred to as "Steam Explosion Pulping Process" or "S-pulping" has been proposed both for softwoods and hardwoods. In this process, impregnation and cooking conditions were aimed at minimizing yield and brightness loss, optimizing resulting paper properties and decreasing specific refining energy. The steam explosion pulping process consists of the chemical impregnation of chips, short duration saturated steam cooking at temperatures varying from about 180 ° C to 210 ° C, pressure release, refining and bleaching (if necessary).

Kokta et al., Paperi Ja Puu - Paper and Timber 9, 1044-1055 (1989), have shown that the specific refining energy of aspen explosion pulps is at least 50% lower than that of CMP pulp of similar yield and ionic content level, while paper strength increases by up to 50%. Compared at similar Canadian standard freeness (CSF) levels, explosion hardwood pulps (i.e. aspen, maple, hardwood mixtures, eucalyptus) at 90% yield provide similar or better paper properties than commercial low yield (≡ 50%) bleached hardwood pulps.

The major problems accompanying previous processes using explosive decompression are believed to have been the degradation due to the oxidation of wood and acid hydrolysis leading to loss in brightness, deterioration of fibre and paper properties and loss of yield. The approach adopted by this invention is therefore to attempt to curtail hydrolytic and oxidative wood degradation and thereby to protect against loss of yield, brightness and fibre strength. The loss of fibre strength will be particularly great if the degree of polymerization of the cellulose falls below the critical value which is about 500-600. Hydrolytic degradation will also cause yield loss due mainly to degradation of hemi-cellulose.

The present invention provides a process in which additional energy saving and improved paper properties are obtained by pressurizing the reactor with inert gas before explosive decompression.

The process of this invention achieves a positive improvement in the strength of the paper that will be produced from the fibres by increasing the number of hydrophilic groups on the fibre surfaces thereby adding to the potential sites for hydrogen bonding.

The conditions for the optimising of the foregoing objects in accordance with the process of this invention are as follows:

1) The wood fragments, having fibres suitable for paper making, such as chips, are in a form in which thorough chemical impregnation can be achieved in a reasonable time.

2) There is an initial thorough impregnation of the chips or other wood fragments by a preferably alkaline aqueous liquor having at least one agent acting to produce hydrophilic groups and as an antioxidant which is capable of protecting the chips against oxidation and provides hydrophilic groups in the chips during the cooking stage. The same chemical may act as both an agent to produce hydrophilic groups and as an antioxidant or these functions may be performed by separate chemicals. At the end of cooking the pH should preferably not be lower than about 6.0, so that acids released during cooking will be neutralized. Preferably a swelling agent is also used in the case of high density wood.

3) The impregnated chips are cooked using saturated steam in the substantial absence of air at high temperature and pressure.

4) After cooking the reactor is pressurized with cool inert gas: the chips that have been steam cooked and pressurized are subjected to explosive decompression to result in chips which are softened and mostly defibrated. The preferred gas used is nitrogen and the preferred temperature is about 10-50 ° C.

5) The defibrated chips are preferably washed and then, without undue delay, and preferably immediately, refined to provide pulp.

The steps of the process of this invention, which will for convenience be referred to as the improved explosion process, will now be considered in more detail.

The wood fragments

The starting material will normally be chips in which the fibres are of a length suitable for paper making. Shavings could also be used but sawdust would be undesirable, except as a minor part of the total furnish, as the fibres are partially cut.

The chips would also, as is well known, be suitable in the sense of being free from bark and foreign matter.

It is desirable for the purposes of this invention that coarse chips be avoided as otherwise the subsequent impregnation may deposit chemicals only on the chip surface, unless impregnation is carried out for a very long time. Another problem with coarse chips is that cooking would not be complete. It is best to use shredded or thin chips of a 4-8 mm thickness. It has been found that this process is applicable to hardwoods, jack pine and larch, black spruce and douglas fir giving stronger papers at lower refining energy compared with conventional chemi-thermomechanical or chemi-mechanical pulping.

Impregnation

The purpose of impregnation is to protect the chips against oxidation during cooking and during transfer from the cooking vessel to the refiner. It is also an objective to provide a positive increase in strength by developing hydrophilic groups on the fibre surface during steam treatment. This will then provide additional sites for hydrogen bonding.

The preferred anti-oxidant is sodium sulphite, Na_2SO_3, which also forms hydrophilic groups, and which is available at a low cost. It is used to provide a concentration of absorbed chemical of about 1 to 15%. Concentrations below 4% would be used where brightness protection is unimportant and high strength is not required. Where, however, brightness is important the sodium sulphite should be at least 4%. If physical properties are important these will be improved by using a concentration of at least 4% sodium sulphite and will be further improved as the concentration is further increased towards 12%. The concentration of the solution is preferably about the same as the percentage of chemical to be absorbed where there are equal quantities of chips and liquor. For example, using 1000 kg of chips of 50% consistency, that is made up of 500 kg of chips mixed with 500 kg of solution, where the solution is 8% sodium sulphite, results in the sodium sulphite absorbed by the chips being 8% by weight of the total weight of the chips. Of importance is thorough impregnation to distribute the antioxidant evenly rather than depositing it just on the surface. Other antioxidants that can be used are potassium sulphite or magnesium sulphite. Ammonium sulphite could be used if cooking conditions are not severe or with a buffer. Complexing agents such as ethylene diamine tetracetic acid (EDTA), sodium diethylene triaminepentacetate (DTPA), sodium tripolyphosphate (TPF) and other complexing agents known in the art as being usable under alkaline conditions may be added to minimize the catalytic effect of metals such as iron on oxidative degradation.

It is desirable also to use a swelling agent to assist the antioxidant or hydrophilic agent in penetrating the wood and this contributes also to softening the chip. This is of particular value in the case of high density wood. Suitable swelling agents are sodium or potassium hydroxide or ammonium hydroxide or sodium carbonate or sodium bicarbonate which will contribute also to providing hydrophilic groups. Other swelling agents that can be used and which may be desirable as auxiliary swelling agents for high density wood are zinc chloride, sodium chloride, sodium bromide, calcium isocyanate, Schweitzers solution, cupriethylenediamine (C.E.D.) tetraethylammonium hydroxide and dimethyldibenzylammonium hydroxide. The concentration of swelling agent and conditions of swelling must be controlled in such a way as to avoid any dissolution of the hollocellulose. Thus the percentage of swelling agent in the impregnating solution will be in the range of about 1 to 4% depending on the agent and the conditions.

The impregnating solution must be alkaline and have enough free hydroxyl to be able to neutralize the liberated wood acids such as formic acid and acetic acid. Normally the starting pH is about 7.5 or higher and the final pH after steam cooking should be at least 6 or higher.

The time of impregnation at atmospheric pressure in holding tanks typically ranges from about 12 hours to 24 hours at a temperature of about 30 ° C to 60 ° C. Approximately equal weights of chips and of aqueous impregnating solution can be used. For industrial purposes, however, the time may be shortened to an hour or to minutes by impregnating with steam under pressure and at a higher temperature. The pressure should be up to about 1 atmospheric extra pressure at a temperature of about 100 ° C to 110 ° C. The impregnation may be carried out in the substantial absence of air, achieved by replacing air with saturated steam. To improve impregnation the chips should be compressed in advance of impregnation in solutions of the chemicals, sodium sulphite, or sodium sulphite and swelling agent and complexing agent DTPA etc., at a temperature of about 15-50 ° C. Under these conditions, penetration will be achieved in a shorter time, but penetration is what predominantly occurs. There is no significant cooking.

Steam cooking

The impregnated chips are steam cooked at a high temperature and pressure.

Equipment and methods that can be used for preliminary compacting of the impregnated chips, for cooking the chips with steam and for the discharge of the chips under conditions of explosive decompression are described in CA-A-1 070 537 dated January 29, 1980; 1 070 646 dated January 29, 1980; 1 119 033 dated March 2, 1982 and 1 138 708 dated January 4, 1983, all of which were granted to Stake Technology Ltd. The equipment used in the examples was acquired from that company.

The temperature of cooking should be within the range of about 180 ° C to 210 ° C and preferably within the range 190-200 ° C. These temperatures correspond with a pressure of about 10 atmospheres for 180 ° C and about 15.5 atmospheres for 200 ° C. It is these high pressures which make a very important contribution to ensuring excellent penetration of the chips by the cooking liquor.

The cooking may be preceded by steam flushing under low pressure steam at 100 ° C for a short period such as one minute. This is a matter of convenience, in that with a batch reactor the cooking vessel is initially open to the atmosphere, to eliminate air. This air would be disadvantageous in that it would result in oxidation if it were trapped in the cooking vessel. Additional antioxidant may, if desired, be added at this stage. Steam flushing is desirable with a batch reactor but would not be necessary for a continuous reactor.

This preliminary treatment is then followed by cooking for about 30 seconds to 6 minutes and preferably about 1 to 4 minutes.

It has been found that within reasonable limits there is a property improvement by increasing the value of the product of the cooking time and the temperature (K). By increasing this value from 285 to 760 in the case of black spruce at about the same freeness (157-167 ml) the burst index increased from 3.15 to 4.41 k Pa m^2/g and breaking length from 6.3 to 7.6 km and tear from 5.6 to 5.8 mN m^2 /g. Refining energy dropped from 3.2 to 3.1 and brightness dropped from 53.7 to 49.1 (equivalent to 59.7 to 55.1). These figures are adjusted to those that ordinarily would be obtained by using an industrial refiner in place of a laboratory refiner. Impregnation was with 8% sodium sulphite and 1/2% of DTPA.

Pressurization

After cooking, the reactor is pressurized immediately with an inert gas such as nitrogen. The pressurization conducted after cooking with saturated steam is accomplished in order to obtain optimum results as far as paper properties, yield and brightness are concerned. The nitrogen temperature, being well below the cooking temperature, is not likely to increase hydrolysis and decrease cooking yield. The use of nitrogen pressure, varying from about 25 to 50 atm, contributes to even more efficient chip defibration in the subsequent step of pressure release.

Explosive decompression

After cooking the pressure is instantaneously released and the chips are exploded into a release vessel.

If there is to be a delay between release of the chips and refining it is important to cool the chips down by washing them. Washing may also be desirable for the purpose of chemical recovery.

It is desirable to refine the chips immediately after explosive decompression. Otherwise, if the chips are stored some oxidation will occur with resultant loss of brightness. The rapidity with which this will occur depends on how much residual antioxidant is present at that time and on the temperature of the chips and the extent of exposure to oxygen. Preferably, therefore, refining is immediate so that it is unnecessary to incur the cost of excess antioxidant. In any event, undue delay should be avoided. Such delay is regarded as being undue if oxidation takes place to an extent that will materially affect brightness.

The chips resulting from the explosive decompression are softened and partially defibrated.

Refining

Refining in the experiments described below using an atmospheric laboratory refining was conducted at 2% consistency level using a blender coupled with an energy meter model EW 604.

According to A.C. Shaw "Simulation of Secondary Refining" Pulp and Paper Canada 85(6): T152-T155 (1984) the blender results closely match those obtained with industrial refiners. Properties were evaluated after preparing paper sheets according to standard CPPA testing methods.

Refining energies are usually low and can be expected to be in the range of 2.6 to 4 MJ/kg, hardwoods, CSF ≡ 100 ml, which is considerably lower than that of conventional CMP and about 20% lower than that described in Kokta, CA-A-1 230 208 and US-A-4 798 651 (1989).

The following example is provided to illustrate the invention. Properties of paper produced from pulp resulting from the process of the invention are summarised in Tables 1 and 2 and Figures 1, 2 and 3.

EXAMPLE

Chips

Freshly cut and naturally grown aspen trees from the Joliette region of Quebec were debarked, chipped and screened at La Station Forestière Duchesnay, Quebec. Average chip size after screening, was as follows: length 2.5 to 3.75 cm; width: 1 to 2 cm; thickness: 1 to 9 mm with maximum distribution at 5 mm.

Impregnation

150 g of chips (= 50% siccity) were mixed in plastic bags along with 375 g of a solution made up of 8% Na_2SO_3. Time of impregnation: 24 hours; temperature of impregnation: 60 ° C. Liquid/chip ratio during impregnation was equal to 6.

In addition, 0.5% DTPA was used in applied cooking liquors.

Cooking

Explosion pulps have been prepared using vapor phase steam cooking of sulfite pretreated aspen wood chips. Pulps have been prepared with the same 90% yield by using cooking temperatures 190 ° C, 195 ° C and 200 ° C with cooking times 2 minutes, 1.5 minute and 1 minute respectively.

Cooking took place using saturated steam in a laboratory batch reactor built by Stake Tech. Co. Cooking was preceded by one minute steam flushing at atmospheric pressure. After cooking, the pressure was instantaneously released and chips which exploded into the release vessel were washed and cooled down with one litre of tap water, and subsequently refined after being stored in a cold room. The reported amount of steam used for cooking varied from 0.5 to 1 kg of steam for 1 kg of chips. Yield was measured as follows: exploded chips (75 g) were washed with one litre of tap water and subsequently defibrated for 90 seconds in a laboratory blender at 2% consistency. The pulp was washed again with one litre of water, dried at 105 ° C to constant weight and the resulting weights were compared with the initial weight of chips.

Two types of explosion have been used:

a) Ordinary explosion: the chips were exploded after vapor phase cooking. The pressure was proportional to the saturated steam pressure at the cooking temperature. Cooking conditions and properties of the end-product paper are presented in Table 1.

b) Nitrogen explosion: nitrogen was added to the reactor 5 seconds before finishing the cooking process. When the pressure reached 25 atm, the chips were exploded into the release vessel. Cooking conditions and properties of the end-product paper are presented in Table 2.

Refining

Laboratory refining was also done using a domestic blender Osterizer B-8614 at a consistency level of 2%. Defibration and refining energy was measured using a HIOKI model 3181-01 powermeter with an integrator. Specific refining energy was calculated by subtracting blending energy of fully beaten pulp from the total energy needed to defibrate and blend the fibre suspension.

Property evaluation

Paper sheets were prepared and tested according to standard CPPA testing methods on 1.2 g sheets. Brightness (Elrepho) was evaluated on sheets made with deionized water.

Bleaching

Bleaching was carried out using 4% of hydrogen peroxide.

In Table 1, cooking conditions as well as paper properties are provided for ordinary explosion process as defined in Kokta, Can. Pat. 1 230 208 and U.S. Pat. 4 798 651 (1982).

In Table 2, cooking conditions as well as paper properties are provided using the pressurization by nitrogen before explosion, the conditions the subject of the present invention.

The yield of nitrogen exploded pulps has not been decreased by more than 0.4% compared to ordinary exploded pulps.

Refining time and refining energies of nitrogen exploded pulps showed significant savings (about 20%) compared to ordinary exploded pulps.

The brightness of nitrogen exploded pulps in both cases, unbleached and bleached, has not been lowered by more than 1% compared to ordinary exploded pulps.

The nitrogen explosion process seems to be very promising in the field of explosion pulping processes. It allows the preparation of very high yield pulps which are easy to refine; they can be easily bleached to more than 80% MgO brightness by single stage peroxide bleaching and their properties are superior to conventional CMP/CTMP with the same yield.

TABLE 1

ORDINARY EXPLOSION					
COOKING TEMPERATURE (° C)	COOK TIME (min)	FREENESS (ml)	BREAKING LENGTH (km)	TEAR (mNm^2/g)	BURST (kPa m^2/g)
190	2	500	4.50	7.20	1.85
190	2	300	5.05	7.20	2.20
190	2	100	6.45	7.50	3.10
195	1.5	500	3.90	7.20	1.60
195	1.5	300	4.60	7.30	2.05
195	1.5	100	6.60	7.60	3.05
200	1	500	3.45	6.70	1.40
200	1	300	4.65	7.05	1.95
200	1	100	6.45	7.35	2.85

TABLE 2

NITROGEN EXPLOSION					
COOKING TEMPERATURE (° C)	COOK TIME (min)	FREENESS (ml)	BREAKING LENGTH (km)	TEAR (mN m^2/g)	BURST (kPa m^2/g)
190	2	500	4.05	7.35	1.65
190	2	300	5.35	7.50	2.30
190	2	100	7.30	7.75	4.00
195	1.5	500	4.40	8.30	1.95
195	1.5	300	6.05	7.90	2.70
195	1.5	100	7.35	8.00	3.65
200	1	500	4.10	7.90	1.60
200	1	300	5.10	8.00	2.40
200	1	100	6.95	8.15	3.65

Claims

1. A process for producing pulp, comprising:
impregnating wood fragments with a solution capable of providing hydrophilic groups and an antioxidant in the fragments,
steam cooking the impregnated fragments in a reactor with saturated steam at superatmospheric pressure and at a temperature in the range of 180° to 210° C,
further pressurizing the reactor with cool inert gas,
thereafter explosively decompressing the cooked fragments, and
subsequently refining the product to provide the pulp.

2. A process according to claim 1 wherein the inert gas is nitrogen.

3. A process according to claim 2 wherein the pressure of nitrogen is 25 to 50 atmospheres.

4. A process according to claims 2 or 3 wherein the temperature of nitrogen is 10 to 50° C.

5. A process according to any one of claims 1 to 4 wherein the step of impregnating wood fragments is carried out in the substantial absence of air, achieved by replacing air with saturated steam

6. A process according to any one of claims 1 to 5 wherein the solution used for impregnating wood fragments contains sodium sulphite.

7. A process according to any one of claims 1 to 6 wherein the steam cooking is at a temperature of 190° C to 200° C.

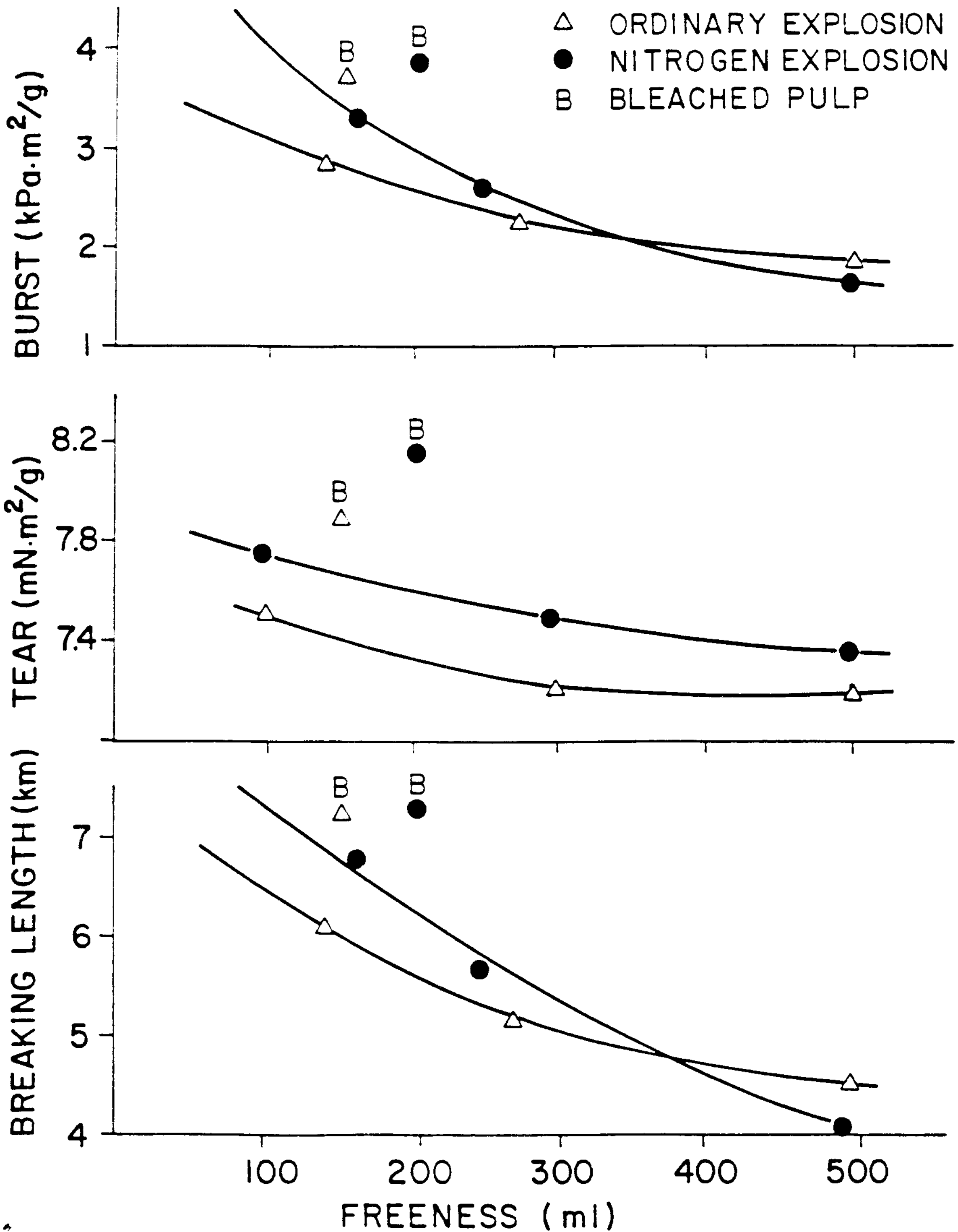
8. A process according to any one of claims 1 to 7 wherein the steam cooking is at a pressure of 10 atmospheres to 15.5 atmospheres.

9. A process according to any one of claims 1 to 8 wherein the steam cooking is for a time of 30 seconds to 6 minutes.

10. A process according to any one of claims 1 to 9 wherein the further pressurizing is for a time of 5 seconds to 2 minutes.

11. A process as substantially herein described in any one of the preceding claims.

STEAM EXPLOSION PULPING: COMPARISON ORDINARY AND NITROGEN EXPLOSION AT 190 °C; 2 MIN; 8% Na_2SO_3
2.5 MPa
L/C = 6



90% YIELD

FIGURE 1

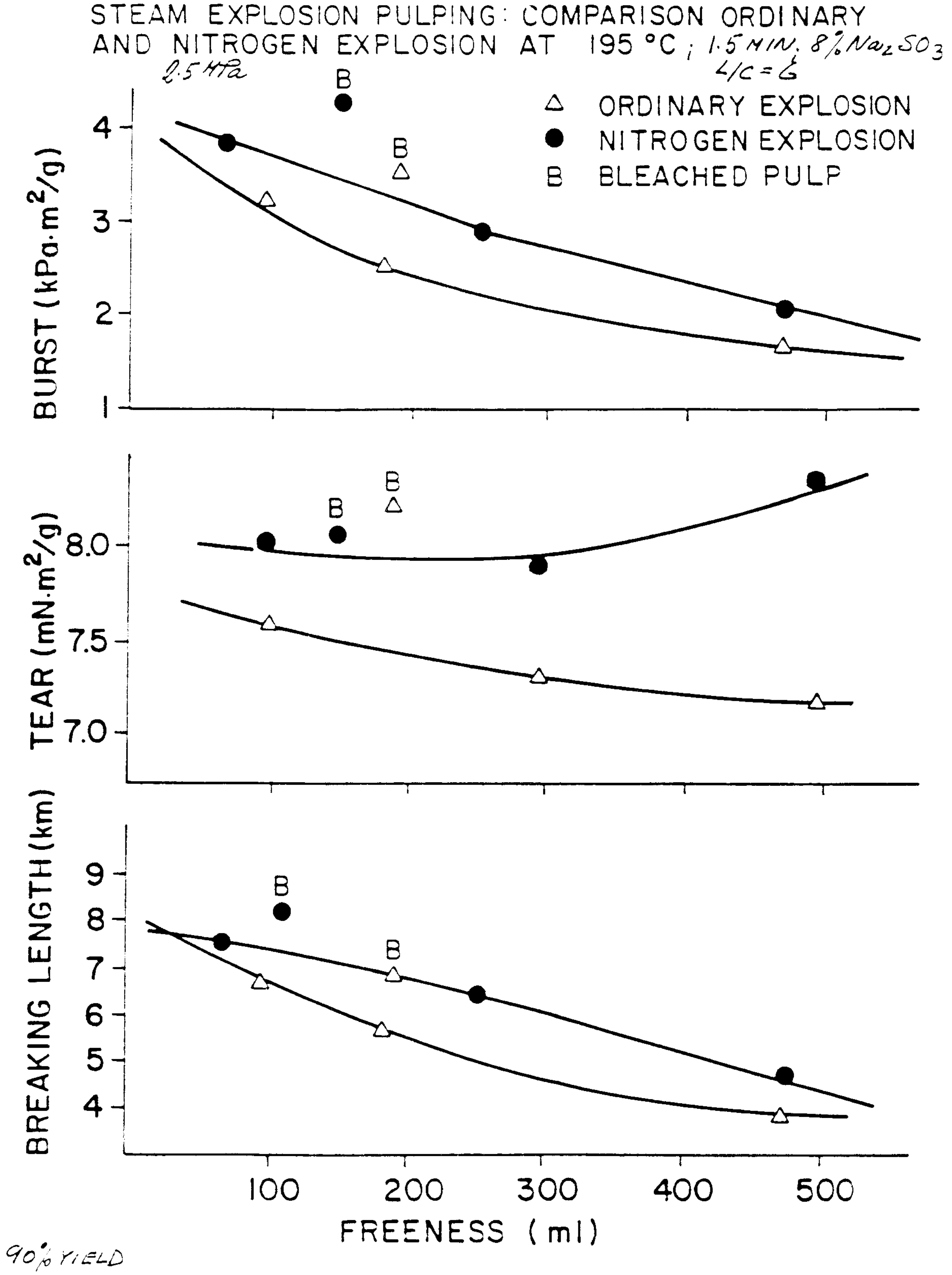
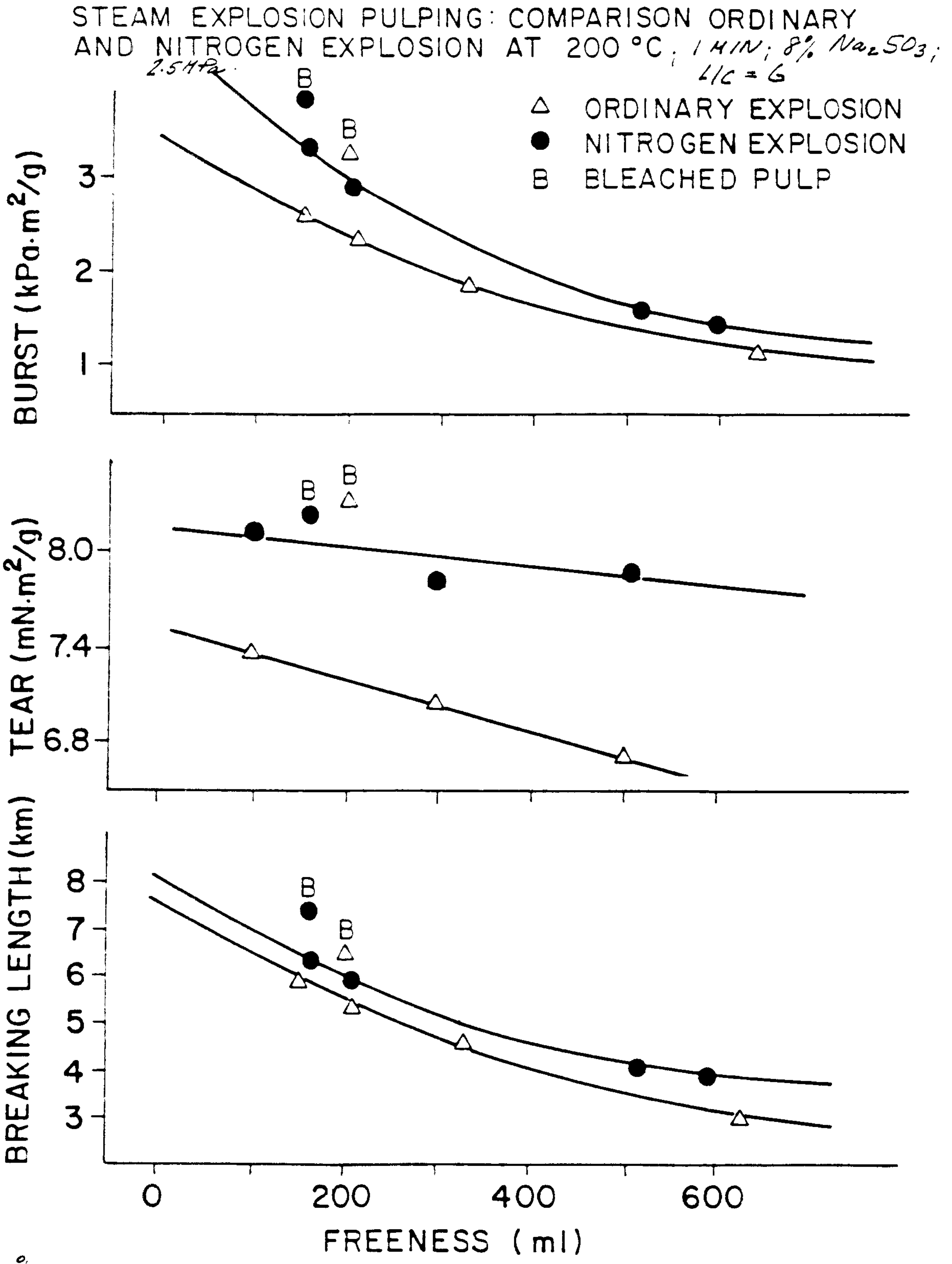

STEAM EXPLOSION PULPING: COMPARISON ORDINARY AND NITROGEN EXPLOSION AT 195 °C ; 1.5 MIN. 8% Na_2SO_3
2.5 MPa
L/C = 6
△ ORDINARY EXPLOSION
● NITROGEN EXPLOSION
B BLEACHED PULP
B
BURST (kPa·m²/g)
1
2
3
4
TEAR (mN·m²/g)
7.0
7.5
8.0
BREAKING LENGTH (km)
4
5
6
7
8
9
100
200
300
400
500
FREENESS (ml)
90% YIELD

FIGURE 2



90% YIELD

FIGURE 3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 31 2833

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-4163687 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION) * column 6, lines 23 - 43 * * column 8, lines 38 - 46 *	1, 6-8, 11	D21B1/36 D21C3/22
A		2, 3	

D,Y	CA-A-1230208 (STAKE TECHNOLOGY LTD.) * the whole document *	1, 6-8, 11	
D,A		5, 9	

A	TAPPI. vol. 64, no. 7, July 1981, ATLANTA US pages 93 - 96; Mamers,H. et al.: "Explosion pulping of bagasse and wheat straw." * page 1, left-hand column, lines 26 - 36 * -----	1, 2, 7	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
D21B D21C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 JULY 1991	BERNARDO NORIEGA F.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

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