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(54) Titre : PROCEDE POUR ELIMINER L'HEMICELLULOSE DE FIBRES CELLULOSIQUES EN UTILISANT UNE
SOLUTION D'AMMONIAC ET DE PEROXYDE D'HYDROGENE
(54) Title: METHOD OF DEGUMMING CELLULOSIC FIBRES

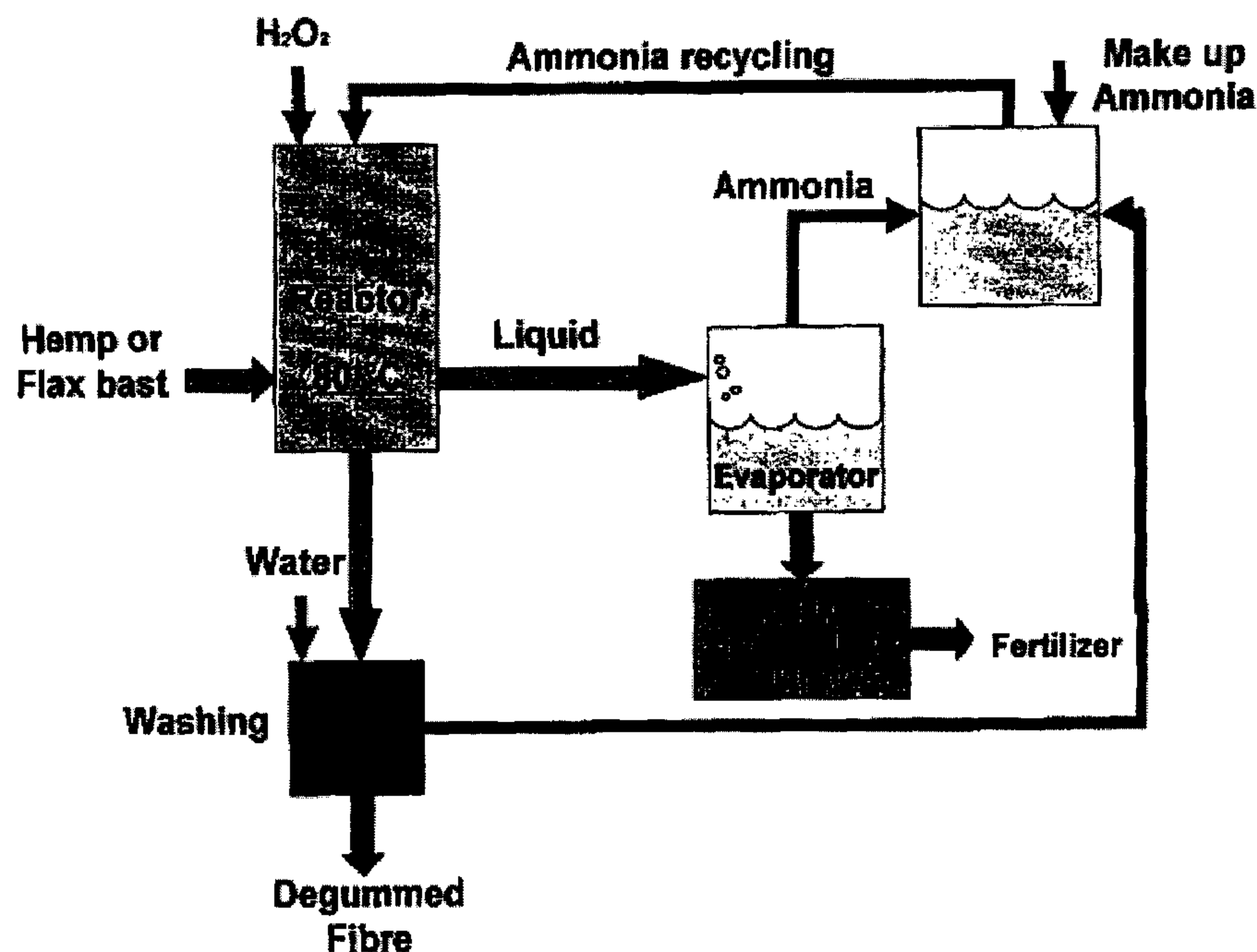
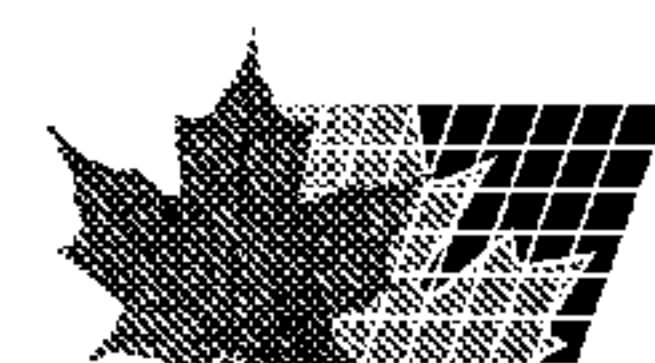


FIGURE 1

(57) Abrégé/Abstract:

A method for increasing the quality of cellulosic fibres used in forming dissolving pulp wherein the hemicellulose content of a pulp is reduced by treating the fibres with a liquor which includes hydrogen peroxide and ammonia.



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(54) Title: METHOD TO REMOVE HEMICELLULOSE FROM CELLULOSIC FIBRES USING A SOLUTION OF AMMONIA AND HYDROGEN PEROXIDE

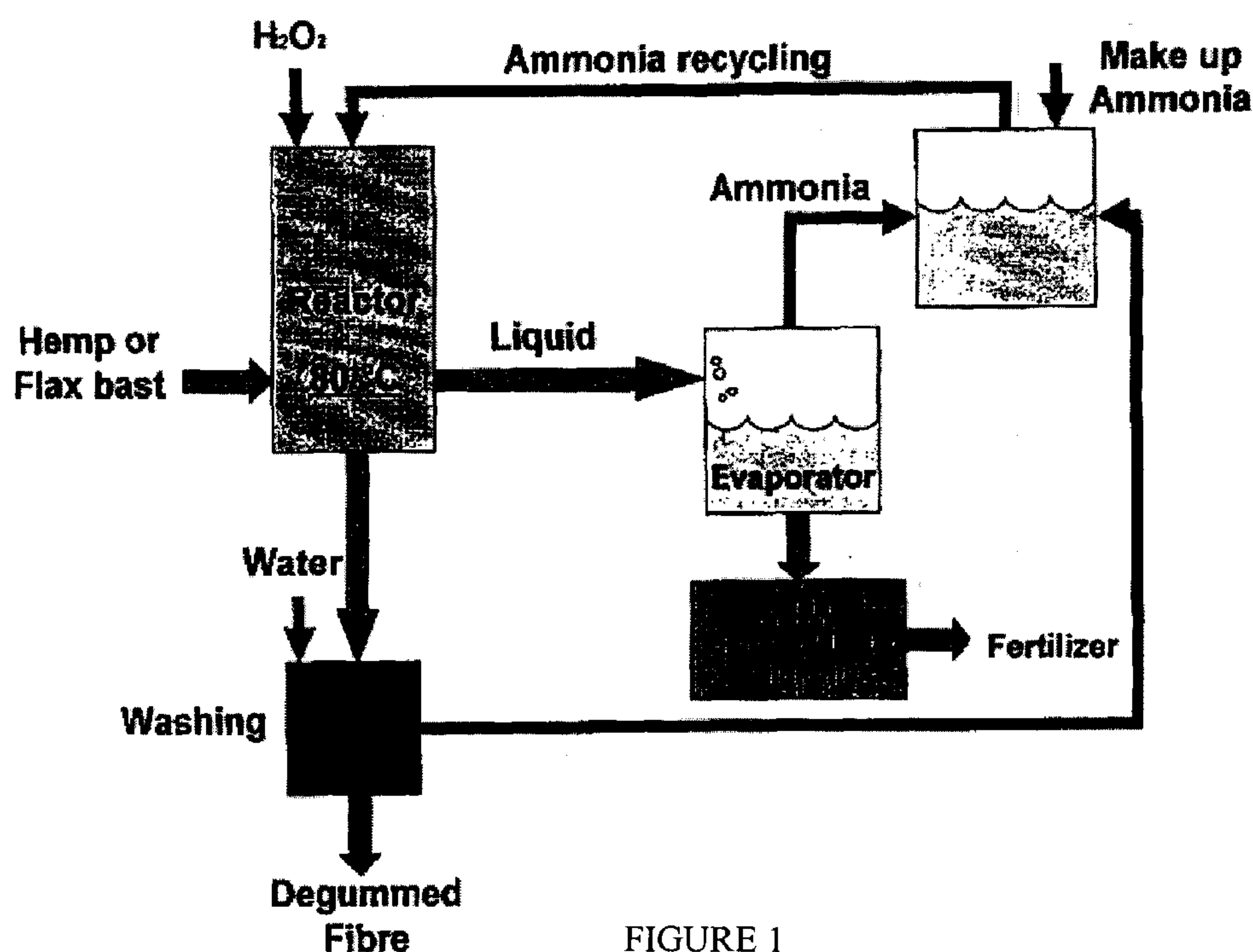


FIGURE 1

(57) Abstract: A method for increasing the quality of cellulosic fibres used in forming dissolving pulp wherein the hemicellulose content of a pulp is reduced by treating the fibres with a liquor which includes hydrogen peroxide and ammonia.

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5 **METHOD OF DEGUMMING CELLULOSIC FIBRES**

Field of the Invention

The present invention relates to a method of degumming or delignifying lignocellulosic fibres, and in particular to a method of producing dissolving pulp fibres.

10 **Background**

Pulp is a generic term for a wide range of technically distinct products resulting from complex manufacturing processes that involve the chemical and/or mechanical treatment of various types of plant material. Wood currently provides the basis for approximately 90% of global pulp production; the remaining 10% begins as straw, bamboo, bagasse, kenaf, flax, 15 hemp, cotton, and the like. Pulp is used predominantly as a major component in the manufacture of paper and paperboard. Smaller quantities of pulp find their way into a diversity of products - rayon, photographic films, cellophane and explosives.

The highest grade of pulp is chemical-grade or dissolving-grade pulp. Dissolving pulp is used in the manufacture of value-added products such as:

- 20 • viscose fiber (rayon) or film, made by dissolving pulp in alkaline carbon disulfide (xanthation) thus forming the xanthate salt as an intermediate product, and forcing the solution through orifices into an acid bath.
- cellulose derivatives such as cellulose acetate, ethyl cellulose, cellulose nitrate (nitrocellulose, guncotton), and carboxymethylcellulose (CMC).

5 Dissolving pulp manufacture usually utilizes kraft or sulfite pulping of wood (both
softwoods and hardwoods), or soda pulping of cotton linters. When pulping wood for
dissolving pulp, the bleached yield is only 32-36% so as to obtain purer pulp. The cellulose
content is commonly 88-93% (for commodity grade viscose), but may be as high as 98% for
more demanding end-uses (eg: tire cord). The contents of extractives, lignin, iron and ash are
10 also low. Viscosity (ie: DP) is another important property, with the actual level depending on
the end-use of the pulp. For commodity grade viscose, the viscosity may be about 350 to
about 550 ml/g. High grade dissolving pulp may exceed 600 ml/g.

To create dissolving pulp, conventional kraft pulping is modified to include a
prehydrolysis stage, before the main cook, where the hemicellulose is hydrolyzed and
15 removed. Dilute acid or alkali, or just direct steam, is used in this prehydrolysis stage. This
additional stage approximately doubles total cooking time, relative to a normal kraft cook. A
cold alkali extraction stage in the bleaching sequence further removes the non-cellulose
components.

Acid sulfite pulping is carried out at a high temperature and low pH to achieve the desired
20 hemicellulose degradation. Bleaching includes a hot alkali extraction stage to further remove
the non-cellulose components.

Some studies have indicated that dissolving pulp may be obtainable from either bleached
hardwood kraft market pulp or high quality wood pulp rich in hardwood fiber. The sequence
included two cold alkali extraction stages with xylanase treatment in between. [Jackson, L.S.

5 *et al.* Production of dissolving pulp from recovered paper using enzymes. TAPPI Journal, March 1998].

These prior art methods of producing dissolving pulp consume large amounts of chemicals and energy, and require complex black liquor recycling processes. A separate bleaching step is required after alkaline degumming.

10 Therefore, there is a need in the art for methods of producing degummed pulp suitable for producing dissolving pulp which mitigates the disadvantages of the prior art.

Summary Of The Invention

In one aspect, the invention comprises a method of degumming cellulosic fibres comprising the step of treating the fibres with a degumming liquor comprising between about 15 5% to about 30% (v:v) aqueous ammonia and between about 0.5% to 3% (on OD fibre) hydrogen peroxide, at a temperature between about 50° to about 200° C, at a consistency of about 3:1 to about 20:1 liquor to solids (v/w). The degumming liquor may further comprise 0% to 10% (on OD fibre) of potassium hydroxide and 0% to 0.2% (on OD fibre) of anthraquinone.

20 In one embodiment, the cellulosic fibres may comprise hardwoods, softwoods, and bast fibre plants, for example, hemp, flax, kenaf, linseed, jute, ramie and other dicotyledonous plants having fibrous phloem, such as cereals, perennial grasses, or legumes.

In one embodiment, the degumming liquor is recovered following degumming, and an aqueous portion is recycled to provide ammonia, and a solid portion is recovered in a waste

5 recovery stream. In one embodiment, the solid portion is recovered and treated to form a fertilizer.

The degummed fibres may be bleached to form dissolving pulp.

In another aspect, the invention comprises a method of forming dissolving pulp from bast fibre plants, comprising the steps of:

10 (a) pulping the plant fibre with a degumming liquor comprising ammonia and hydrogen peroxide;

(b) recovering and recycling an aqueous portion from step (a);

(c) recovering the pulped fibres and bleaching to produce dissolving pulp.

The bast fibre plant fibres may comprise hemp, flax, kenaf, linseed, jute, or ramie fibres.

15 **Brief Description Of The Drawings**

In the drawings, like elements are assigned like reference numerals. The drawings are not necessarily to scale, with the emphasis instead placed upon the principles of the present invention. Additionally, each of the embodiments depicted are but one of a number of possible arrangements utilizing the fundamental concepts of the present invention. The
20 drawings are briefly described as follows:

Fig. 1 is a schematic view of one embodiment of the present invention.

Detailed Description Of Preferred Embodiments

5 The present invention relates to methods of degumming cellulosic fibres, and in particular
to a method of producing high quality dissolving pulp. When describing the present
invention, all terms not defined herein have their common art-recognized meanings. To the
extent that the following description is of a specific embodiment or a particular use of the
invention, it is intended to be illustrative only, and not limiting of the claimed invention. The
10 following description is intended to cover all alternatives, modifications and equivalents that
are included in the spirit and scope of the invention, as defined in the appended claims.

In general, the present invention comprises a method of degumming cellulosic fibres using
ammonia. The degummed fibres may then be bleached using processes well known in the art,
such as chlorine bleaching, elemental chlorine-free ("ECF") bleaching or total chlorine-free
15 ("TCF") bleaching. Given the environmental benefits of ECF and TCF bleaching, preferred
embodiments use those technologies.

In one embodiment, the degumming method is used for cellulosic fibres such as
hardwoods, softwoods, and bast fibre plants, for example, hemp, flax, kenaf, linseed, jute,
ramie and other dicotyledonous plants having fibrous phloem, such as cereals, perennial
20 grasses, or legumes. In one embodiment, the cellulosic fibres comprise hemp or flax fibres.

Methods of separating bast fibre from plant stalks are well known in the art, and need not
be further described herein. One exemplary method of decortivating bast fibre plants is
described in Applicant's co-pending U.S. Patent Application, filed on May 23, 2008 and
entitled "Decortication Process".

5 In the present invention, the inventors have surprisingly found that milder conditions than that found in the prior art, may still result in high quality dissolving-grade pulp.

In one embodiment, the separated bast fibres are mixed in a reactor (10) with ammonia at an elevated temperature. In one embodiment, ammonium hydroxide is used in a concentration of about 5% to 30% by volume, and at a temperature which is between about 50° C to about
10 200° C. Preferably, the temperature is a temperature between about 90° to about 150°, for example, 90° C, 100° C, 120° C, or 150° C. In one embodiment, an amount of a chlorine-free bleaching agent, such as hydrogen peroxide, is used to simultaneously bleach the fibres. This ammonia-peroxide degumming process may take place for about 1 hour to 6 hours at a consistency of about 3:1 to about 20:1 liquor-to-solids ratio (v:w). Those skilled in the art
15 may determine suitable conditions by varying these parameters without undue experimentation. As is well known, increase in severity of one parameter may allow for reduction in the others. For example, the use of higher temperatures or higher concentrations of ammonia may allow reduced cook time. Alternatively, lower concentrations of ammonia may require higher temperatures or cook time to achieve similar results.

20 The amount of hydrogen peroxide is less than 3%, preferably less than about 2%, and most preferably less than about 1% (by weight of oven dry (OD) fibre).

In one embodiment, an alkali such as potassium hydroxide (KOH), potassium carbonate, or magnesium hydroxide may be added to the degumming liquor in a concentration of 0% to about 10% (on OD fibre). The degumming liquor may further comprise 0% to 0.2% (on OD
25 fibre) of anthraquinone. Both the alkali and anthraquinone aids in delignification of the

5 cellulosic fibres, and may therefore be preferable for processing more lignified material, such as wood fibres and cereal straw.

After pulping and degumming in the reactor, in one embodiment, the liquids are recovered and sent to an evaporator (20) where the ammonia is recovered to an ammonia recycling tank (30) which is used as the source of ammonia for the reactor (10). A make-up source (40) of
 10 ammonia is provided. The solids remaining from the evaporator (20) comprise lignin and hemicellulose, with trace ammonia, and are removed to solids recovery tank (50) and may be processed into fertilizer in a waste recovery stream (60).

The pulped and degummed fibres are then washed with water in washing tank (70), in one embodiment resulting in a neutral pH, and the resulting fibres are then sent for bleaching (80).
 15 The wash water will contain ammonia and peroxide and may then be recycled to the ammonia recycling tank (30).

In one embodiment, in a method of producing dissolving pulp, the degummed fibres are then bleached in a TCF or an ECF bleaching process. For example, the fibres may be bleached in a three or four stage ECF process followed by a cold alkaline extraction.
 20 Exemplary conditions of one embodiment are shown below in Table 1:

Table 1

Bleaching stage	Pulp cons.	Temp.	Retention time	Target pH	ClO ₂	NaOH	H ₂ O ₂
	%	°C	min		% on OD fibre	% on OD fibre	% on OD fibre
D ₀	10 to 15	70-80	40-90	2.5	1-7		
E _p	10 to 15	70-80	60-120	11		0.5-1	0.5-1

D ₁	10 to 15	70-80	90-150	4	0.5-2
D ₂	10 to 15	70-80	90-150	4	0.5-2
E*	3 to 15	0-40	30-90		

* NaOH concentration at the cold alkaline extraction stage was 10% w/w.

5 "D" refers to use of chlorine dioxide

"E_p" refers to an alkaline extraction with hydrogen peroxide.

"E" refers to an alkaline extraction

10 In one embodiment, an ECF process is preferred as it is believed the chlorine dioxide dissolves non-bast fibres in the bast fibre feedstock.

The resulting dissolving pulp is of high quality. Dissolving pulp from a bast fibre plant such as hemp may produce yield of greater than 55%, with brightness greater than about 92 % ISO, with alpha cellulose content in excess of 98% and viscosity of more than 650 ml/g is achievable with the methods of the present invention.

15 EXAMPLES

In the examples provided below, "AP pulping" refers to ammonia peroxide pulping, the abbreviation "L:S" refers to the liquid to solids ratio, the abbreviation "AQ" refers to the anthraquinone content and the abbreviation "OD" refers oven-dry.

20 EXAMPLE 1

AP pulping of hemp bast fibre at 150 °C cooking temperature

Table 1-1. AP pulping conditions

NH ₄ OH Concentration in cooking solution	Cooking temperature	Time to cooking temperature	Time at cooking temperature	L:S	H ₂ O ₂	KOH	AQ
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% w/w	°C	min	min	v/w	% on OD fibre	% on OD fibre	% on OD fibre
20	150	40	60	10:1	1	5	0.2

5

Table 1-2. ECF bleaching conditions

Bleaching stage	Pulp cons.	Temp.	Retention time	Target pH	ClO ₂	NaOH	H ₂ O ₂
	%	°C	min		% on OD fibre	% on OD fibre	% on OD fibre
D ₀	10	70	60	2.5	5		
E _p	10	80	90	11		0.8	0.5
D ₁	10	80	120	4	1		
D ₂	10	80	120	4	1		
E*	3	25	60				

* NaOH concentration at the cold alkaline extraction stage was 10% w/w.

Table 1-3. Properties of the hemp bast fibre dissolving pulp

Brightness	Viscosity	Acetone extractives	R18	R10	Alpha- cellulose	Ash	Pulp yield
% ISO	ml/g	%	%	%	%	%	%
92.08	658.51	0.06	99.11	98.25	98.67	0.05	55.52

10

EXAMPLE 2**AP pulping of hemp bast fibre at 90 °C cooking temperature**

15

Table 2-1. AP pulping conditions

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NH ₄ OH Concentration in cooking solution	Cooking temperature	Time to cooking temperature	Time at cooking temperature	L:S	H ₂ O ₂	KOH	AQ
% w/w	°C	min	min	v/w	% on OD fibre	% on OD fibre	% on OD fibre
20	90	40	120	10:1	1	5	0.2

5

Table 2-2. ECF bleaching conditions

Bleaching stage	Pulp cons.	Temp.	Retention time	Target pH	ClO ₂	NaOH	H ₂ O ₂
	%	°C	min		% on OD fibre	% on OD fibre	% on OD fibre
D ₀	10	70	60	2.5	5		
E _p	10	80	90	11		0.8	0.5
D ₁	10	80	120	4	2		
E*	3	25	60				

* NaOH concentration at the cold alkaline extraction stage was 10% w/w.

Table 2-3. Properties of the hemp bast fibre dissolving pulp

Brightness	Viscosity	Acetone extractives	R18	R10	Alpha- cellulose	Ash	Pulp yield
% ISO	ml/g	%	%	%	%	%	%
92.80	785.94	0.02	98.56	98.10	98.54	0.06	56.55

10 Several publications or patents are referenced in this application in order to more fully describe the state of the art to which this invention pertains. Where permitted, the disclosure of each of these publications is incorporated by reference in the present specification as though set forth herein in full.

- 5 The word "comprising" is used herein in a non-limiting sense, and shall mean "including, without limitation or exclusion of other alternatives".

5 **WHAT IS CLAIMED IS:**

1. A method of degumming cellulosic fibres comprising the step of treating the fibres with a degumming liquor comprising between about 5% to about 30% (v:v) aqueous ammonia and between about 0.5% to 3% (on OD fibre) hydrogen peroxide, at a temperature between about 50° to about 200° C, at a consistency of about 3:1 to about 20:1 liquor to solids (v/w).
- 10 2. The method of claim 1 wherein the degumming liquor further comprises potassium hydroxide.
3. The method of claim 1 or 2 wherein the degumming liquor further comprises anthraquinone.
4. The method of claim 1 wherein the degumming liquor is recovered following
15 degumming, and is treated to separate it into an ammonia stream for reuse in the process and a solid fraction.
5. The method of claim 4 wherein the solid portion is recovered and treated to form a fertilizer.
6. The method of claim 1 further comprising the step of bleaching the degummed fibres to
20 form dissolving pulp.
7. The method of claim 1 wherein the cellulosic fibres comprise bast fibre plant fibres.

- 5 8. The method of claim 7 wherein the bast fibre plant is one of hemp, flax, kenaf, linseed, jute, or ramie.
9. The method of claim 8 wherein the bast fibre plant is hemp.
10. The method of claim 8 wherein the bast fibre plant is flax.
11. The method of claim 8 wherein the bast fibre plant is kenaf.
- 10 12. The method of claim 1 wherein the cellulosic fibres comprise wood fibre, cereal straw fibre, perennial grass fibre, or legume fibre.
13. The method of claim 6 wherein the bleaching step comprises an ECF or TCF bleaching step.
14. A method of forming dissolving pulp from bast fibre plants, comprising the steps of:
- 15 (a) pulping the plant fibre with a degumming liquor comprising ammonia and hydrogen peroxide;
- (b) recovering and recycling an aqueous portion from step (a);
- (c) recovering the pulped fibres and bleaching to produce dissolving pulp.
15. The method of claim 14 wherein the degumming liquor comprises about 5% to about
- 20 30% (v:v) aqueous ammonia and between about 0.5% to 3% (on OD fibre) hydrogen peroxide.

- 5 16. The method of claim 14 wherein the degumming step takes place at a temperature between about 50° to about 200° C, at a consistency of about 3:1 to about 20:1 liquor to solids (v/w).
17. The method of claim 13 wherein the final bleaching step comprises an ECF or TCF bleaching process.

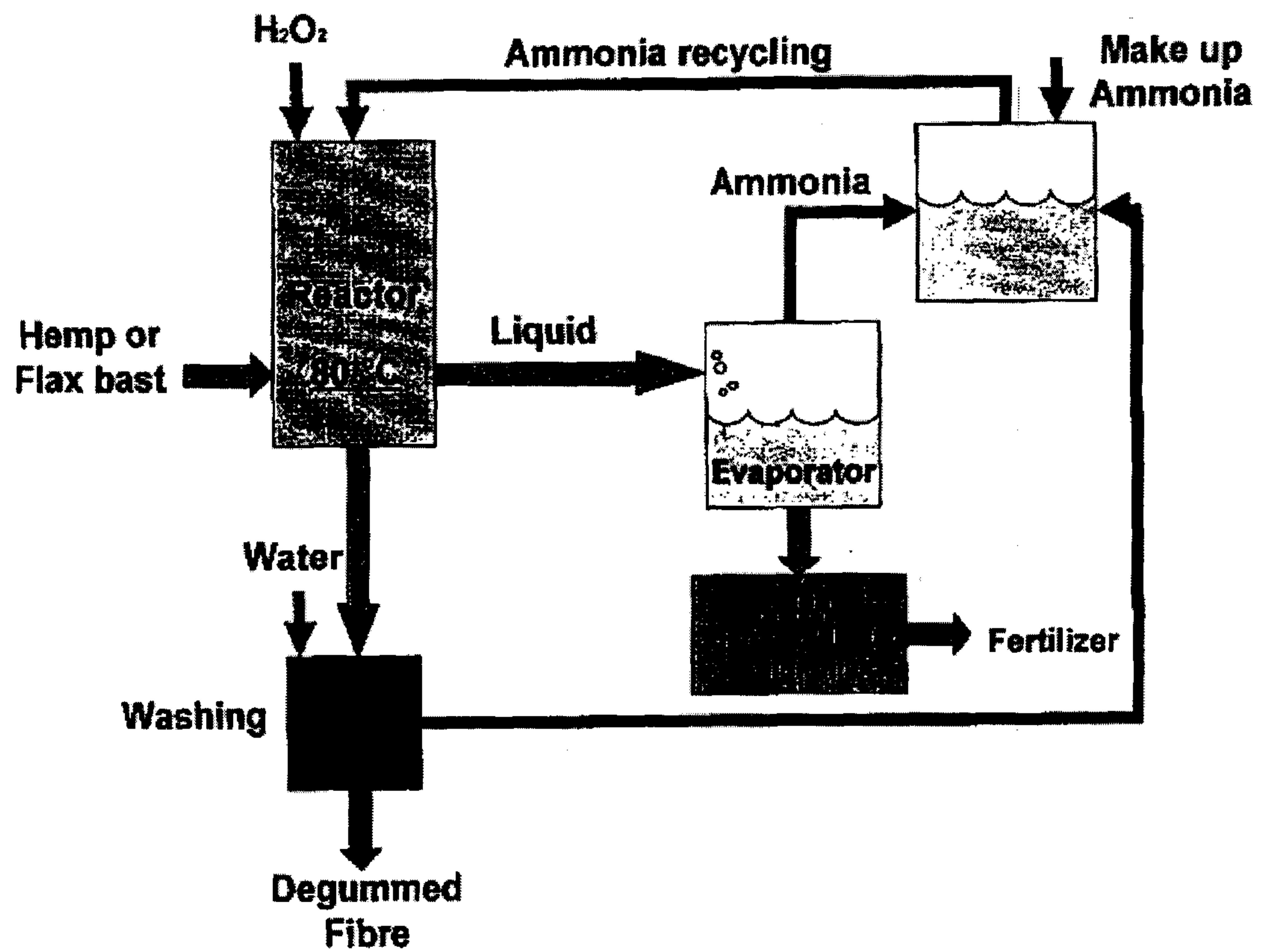


FIGURE 1

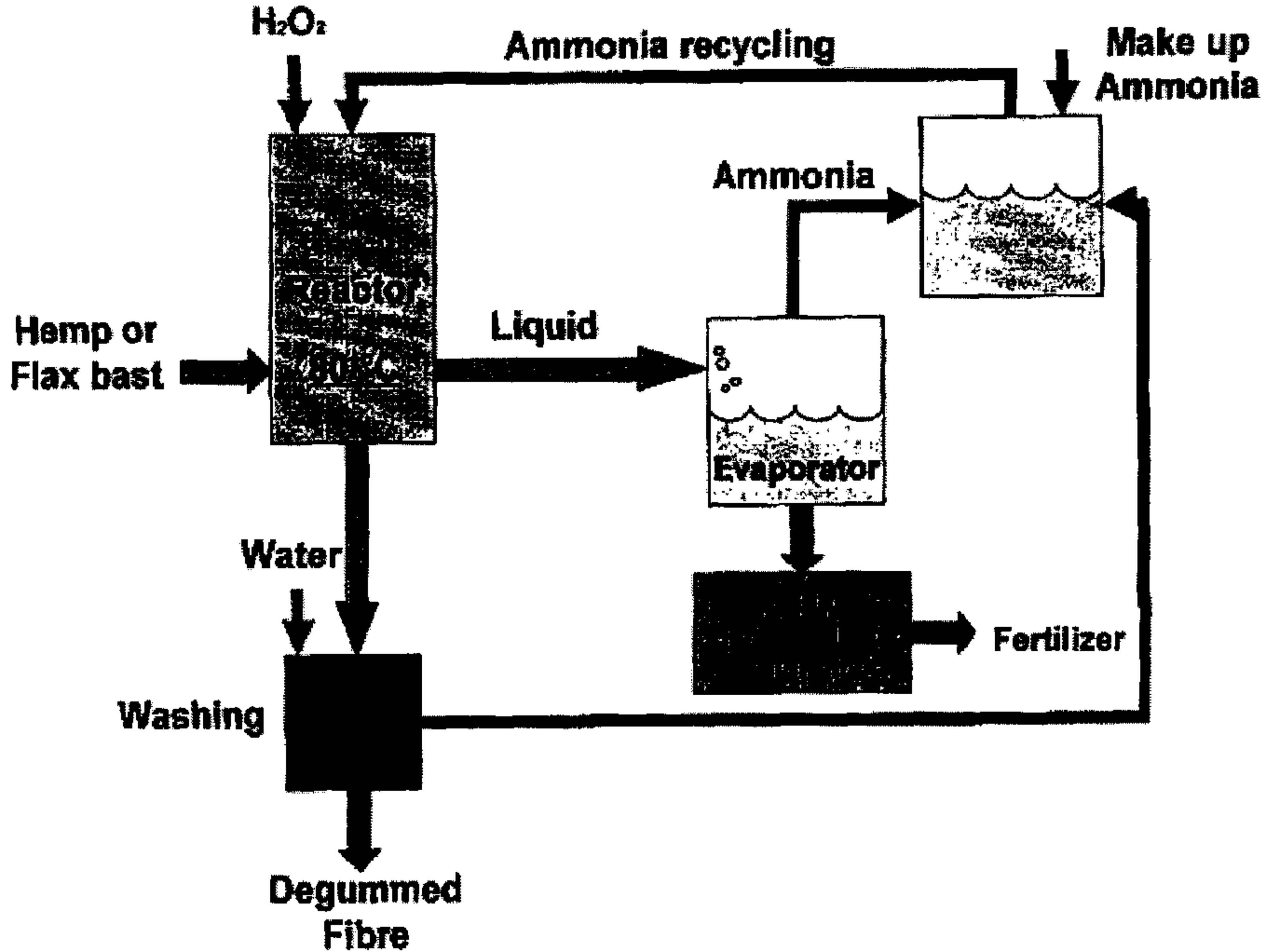


FIGURE 1