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(54) Titre : CELLULOSE II SULFATEE CRISTALLINE ET SA PRODUCTION PAR HYDROLYSE DE LA CELLULOSE
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(54) Title: CRYSTALLINE SULPHATED CELLULOSE II AND ITS PRODUCTION FROM SULPHURIC ACID
HYDROLYSIS OF CELLULOSE

(57) **Abrégé/Abstract:**

A method for producing crystalline sulphated cellulose II materials with relatively low degree of polymerization from spent liquors of sulphuric acid (H_2SO_4) hydrolysis of cellulose has been discovered. The method involves: 1) separating the spent liquors from the hydrolysed, acid-insoluble, cellulose I materials by dilution from, for example, a 64% H_2SO_4 hydrolysis medium to a residual sulphuric acid concentration of 10-50% with 0-40% H_2SO_4 , followed by settling (or centrifuging) and decanting; 2) adding the diluted spent liquors to water or heating the diluted spent liquors at 30-80°C for ≤ 48 h; and 3) recovering the recrystallized sulphated cellulose II materials with relatively low degree of polymerization either by filtration and washing or by washing and freeze drying. The method can be used to concurrently produce both crystalline, sulphated cellulose I and the crystalline, sulphated cellulose II materials.



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CRYSTALLINE SULPHATED CELLULOSE II AND ITS PRODUCTION FROM SULPHURIC ACID HYDROLYSIS OF CELLULOSE

TECHNICAL FIELD

5 This invention relates to crystalline sulphated cellulose II and its production especially from the sulphuric acid hydrolysis of cellulose, the invention also relates to the concurrent production of crystalline, sulphated cellulose I and sulphated cellulose II materials.

10 BACKGROUND ART

Cellulose is the most abundant biopolymer on earth. It is the main component of higher plant cell walls, and it is also formed by some algae, fungi, bacteria, and a group of invertebrate marine animals, the tunicates [See reference by French et al.]. Native cellulose or cellulose from pulping of lignocellulosic materials is fibrous and consists
15 of crystalline and amorphous domains of 1,4-linked β -D-glucose. The crystal structures (polymorphs) of cellulose vary depending on the source of cellulose and the method for its isolation. Because of the existence of various polymorphs, native cellulose has been named cellulose I in respect to its crystalline lattice. Various chemical and thermal treatments can change the lattice of cellulose I and generate other
20 crystalline polymorphs. In terms of industrial applications, the cellulose II polymorph is the most important. It can be obtained by a transformation in the solid state such as in the mercerization process, or from regeneration from dissolved cellulose. Because the lattice of cellulose II is thermodynamically more stable, it cannot be converted back to cellulose I. One common method to characterize cellulose polymorphs is by X-ray
25 diffraction studies. The major peaks in the X-ray diffractograms of crystalline cellulose materials are associated with reflections from the 101, 10 $\bar{1}$ and 002 planes (with increasing 2θ values) corresponding to spacings of 6.01, 5.35 and 3.94 Å in the case of cellulose I and of 7.19, 4.42 and 4.06 Å in the case of cellulose II [See reference a) by Atalla and Nagel]. Native cellulose (cellulose I) derived from wood pulps typically
30 shows poor resolution of the 101 and 10 $\bar{1}$ peaks (peaks with lower 2θ values than the

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002 peak). When cellulose I is converted to cellulose II by mercerization, an increase of 101 spacing and a decrease of 10 $\bar{1}$ spacing occur, which leads to a lower 2 θ value for the 101 peak and a higher 2 θ value for the 10 $\bar{1}$ peak for the mercerized material (cellulose II).

- 5 Hydrolysis of cellulose with sulphuric acid, H₂SO₄, in an aqueous medium under carefully controlled conditions gives cellulose whiskers or nanocrystals with excellent reinforcing ability in polymer nanocomposites [See references by Favier et al., and by Samir et al.]. Hydrolysis of cellulose with 64% H₂SO₄ at 45°C for 20 minutes – 4 h, 65°C for 15 minutes, or 70°C for 10 minutes, introduces negatively charged sulphate
10 groups on cellulose microcrystallites and gives the microcrystallite suspensions that form, at sufficiently high concentrations, an ordered, chiral nematic liquid crystalline phase [See references by Revol et al., and by Dong et al.]. However, the yields of the cellulose microcrystallites that are capable of forming stable colloidal suspensions are only 34.4-48.1%.
- 15 Sulphate group can also be introduced to cellulose by treatment of cellulose with sulphur trioxide, SO₃ in N,N-dimethylformamide (DMF) [See reference by Schweiger]. Various methods for manufacturing sulphated cellulose materials using sulphur trioxide, SO₃ or Lewis base-SO₃ complex as the sulphating agent have been described in the patent literatures (See US Pat. No. 4,064,342; 4,141,746; and 4,389,523). All
20 these methods involve also the use of an organic reagent such as amine and/or an organic dispersant or solvent.

West and Westland have described various methods for making superabsorbent polymers including superabsorbent cellulose (See US Pat. Application Publication 20030045707 A1). One method for making the said superabsorbent cellulose comprises
25 sulfating a cellulosic material with sulfuric acid, dissolving the sulfated cellulose in aqueous medium and precipitating the sulfated cellulose by adding a non-aqueous material (solvent) to the aqueous medium. Another method for making the said superabsorbent cellulose comprises sulfating a cellulosic material with sulfuric acid, dissolving the sulfated cellulose in aqueous medium, and regenerating the sulfated
30 cellulose from the aqueous medium by drying off the water.

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The content of sulphate groups introduced to the cellulose whiskers, nanocrystals or microcrystallites after the sulphuric acid hydrolysis of cellulose is usually assessed by sulphur elemental analysis or by conductometric titration of the materials. Sulphur (S) contents of 0.50-0.75% have been obtained on the microcrystallites obtained from 64%
5 H₂SO₄ hydrolysis of Whatman No. 1 filter paper powder, while a sulphate group content of up to 393 mmol/kg which corresponds to a S content of 1.26% has been reported on the nanocrystals obtained with a yield of 23% and from the hydrolysis of Norway spruce microcrystalline cellulose (MCC) using 64.8% H₂SO₄ at 80°C for 10 min [See reference by Bondeson, et al.].

10 Hydrolysis of bleached softwood kraft pulp or bacterial cellulose with 65% H₂SO₄ at 40 or 70°C has been shown to give cellulose microcrystals or nanocrystals with the cellulose I polymorph [See references by Araki et al., and by Grunert and Winter].

Commercial production of cellulose II from cellulose I is achieved by the viscose method or the cuprammonium method [See reference by Sasaki et al.]. Laboratory
15 preparation of cellulose II from cellulose I has been achieved by conversion of cellulose I to amorphous cellulose by grinding in a vibrating ball mill, and then by recrystallization of the amorphous cellulose by heating with H₂O [See reference by Hermans and Weidinger]. Atalla and Nagel have prepared cellulose II by dissolution of cellulose powder in 85% phosphoric acid, H₃PO₄, and then by slow addition of the
20 dissolved cellulose solution into H₂O at room temperature [See reference a) by Atalla and Nagel]. Atalla and Nagel have also prepared cellulose II with higher crystallinity by mercerizing MCC with 23% NaOH and then by slow dilution of the mercerizing mixture with H₂O and washing of the mixture at higher temperatures such as 80°C [See reference b) by Atalla and Nagel]. Gert has reported the preparation of cellulose II by
25 swelling of cellulose or MCC in 68% nitric acid, HNO₃, and then regenerating through pressing out the acid from the swollen cellulose, diluting with H₂O to ~12% HNO₃ concentrating, heating, filtering and washing [See reference by Gert]. More recently, Sasaki et al. have described the preparation of cellulose II by solubilization of MCC in sub- or super-critical H₂O at 320-400°C (25-33 MPa), and then precipitation by
30 decanting into H₂O at 20°C [See reference by Sasaki et al.].

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Prior to the present invention, however, no soluble, sulphated cellulose has been recrystallized or recovered by simple addition of a solution of soluble, sulphated cellulose to water. In addition, no sulphated cellulose II has been isolated. Furthermore, no cellulose materials have been recovered from the spent liquors of
5 H₂SO₄ hydrolysis of cellulose.

DISCLOSURE OF THE INVENTION

This invention seeks to provide crystalline, sulphated cellulose II with relatively low degree of polymerization (DP).

10 This invention also seeks to provide a method for producing crystalline, sulphated cellulose II.

Further, this invention seeks to provide a process for producing crystalline, sulphated cellulose materials, especially crystalline, sulphated cellulose I from the sulphuric acid hydrolysis of cellulose, and concurrently crystalline, sulphated cellulose II, more
15 especially from the spent liquor of sulphuric acid hydrolysis of cellulose.

Still further, this invention seeks to provide a process for producing crystalline, sulphated cellulose II with relatively low degree of polymerization (DP).

In accordance with one aspect of the invention there is provided crystalline, sulphated cellulose II having a relatively low degree of polymerization (DP).

20 In accordance with another aspect of the invention there is provided a method for producing crystalline, sulphated cellulose II comprising: diluting a spent liquor from the sulphuric acid hydrolysis of cellulose, with an aqueous diluent, separating a diluted spent liquor from an acid-insoluble, crystalline sulphated cellulose I material, and generating crystalline, sulphated cellulose II from the separated, diluted spent liquor.

25 In accordance with still another aspect of the invention there is provided a process for producing crystalline, sulphated cellulose materials comprising:

forming an acid-insoluble, sulphated cellulose I material and a spent liquor from sulphuric acid hydrolysis of cellulose, diluting said spent liquor with an aqueous

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diluent, separating a diluted spent liquor from said acid-insoluble, sulphated cellulose material, generating crystalline, sulphated cellulose II from the separated, diluted spent liquor, and generating crystalline, sulphated cellulose I from the separated, acid-insoluble, sulphated cellulose material.

- 5 In accordance with yet another aspect of the invention there is provided a process for producing crystalline, sulphated cellulose II having a relatively low degree of polymerization (DP) comprising:

dissolution of cellulose in concentrated sulphuric acid to form a solution of dissolved cellulose material comprising sulphated cellulose material, and generating crystalline,
10 sulphated cellulose II from said solution by dilution of said solution with an aqueous diluent.

It has now been discovered that crystalline sulphated cellulose II with relatively low degree of polymerization (DP) can be isolated from spent liquors of H_2SO_4 hydrolysis of cellulose such as fully-bleached kraft pulp fibres. The isolation method involves: 1)
15 separating the spent liquors from the hydrolysed, acid-insoluble cellulose I materials by dilution from, for example, a 64% H_2SO_4 hydrolysis medium to a residual H_2SO_4 concentration of 10-50% with 0-40% H_2SO_4 , followed by settling (or centrifuging) and decanting; 2) adding the diluted spent liquors to water or heating the diluted spent liquors at 30-80°C for ≤ 48 h; and 3) recovering the precipitated sulphated cellulose II
20 materials with relatively low DP either by filtration and washing or by washing and freeze drying. The method can be used to concurrently produce both crystalline, sulphated cellulose I and crystalline, sulphated cellulose II materials with relatively low DP.

It has also been discovered that crystalline sulphated cellulose II with relatively low DP
25 can be isolated from dissolved cellulose solutions in sulphuric acid, added to a known volume of deionized (DI) H_2O over a known period of time at a given temperature (20-80°C).

The crystalline sulphated cellulose II materials with relatively low DP of the present invention can be used as potential antiviral agents such as an anti-human-
30 immunodeficiency-virus (anti-HIV) agent, or multifunctional excipients (a binder, filler

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and disintegrant) for the production of drug tablets or capsules. They may be used for the microencapsulation of biological objects/living cells in the treatment of various diseases such as diabetes. They can also be used for the production of films and fibres, or as strengthening/reinforcing components for the production of polymer nanocomposites or novel paper products.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 Flow diagram of the isolation of crystalline, sulphated cellulose I and crystalline, sulphated cellulose II materials according to the current invention;

10 **FIG. 2** X-ray diffractograms of the acid-insoluble material (— —) showing a cellulose I diffraction pattern and the recrystallized material from the spent liquor (—) showing a cellulose II diffraction pattern;

FIG. 3 X-ray diffractograms of the acid-insoluble material (— —) showing a cellulose I diffraction pattern and the recrystallized material from the spent liquor (—) showing a cellulose II diffraction pattern;

FIG. 4 X-ray diffractogram of the recrystallized material from the clear, dissolved cellulose solution after hydrolysis with 72% H_2SO_4 , showing a cellulose II diffraction pattern.

20 DETAILED DESCRIPTION OF THE INVENTION

The H_2SO_4 hydrolysis of cellulose to form cellulose whiskers, microcrystallites or nanocrystals is typically conducted by mixing the cellulose with concentrated (~64%) H_2SO_4 at a temperature of 45-65°C. The minimum hydrolysis time needed to produce the microcrystallites at this concentration is 20 minutes at 45°C and 15 minutes (i.e. 0.25 h) at 65°C [See reference by Dong et al.]. The hydrolysis produces the acid-insoluble, sulphated cellulose whiskers, microcrystallites or nanocrystals by degrading and solublizing the structurally more vulnerable amorphous domains of cellulose. The spent liquors from such H_2SO_4 hydrolysis consist of residual H_2SO_4 and the soluble

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cellulose degradation products and other by-products of the hydrolysis. The acid-insoluble, sulphated cellulose materials with yields typically lower than 50% are separated from the spent liquors by settling (or centrifugation), decanting and repeated washing or by filtration and washing. No method has been reported in the literature to
5 recover cellulose II from the spent liquors of this type of hydrolysis.

According to the present invention, diluting the spent liquors from concentrated (56-68%) H_2SO_4 hydrolysis of cellulose with an aqueous diluent, more preferably 0-40% H_2SO_4 solution, separating the diluted spent liquors from the acid-insoluble, sulphated cellulose materials, and adding the diluted spent liquors to water (or diluting the spent
10 liquors with water) or heating them at 30-80°C for ≤ 48 h will allow the generation, more specifically, recrystallization and isolation of sulphated cellulose II materials with relatively low DP (typically $\text{DP} \leq \sim 60$) from the spent liquors. The separated, acid-insoluble, sulphated cellulose materials can be, if needed, further hydrolyzed, without addition of extra H_2SO_4 or with the addition of H_2SO_4 to bring the H_2SO_4 acid
15 concentration up to 64-68%, to give highly-crystalline, sulphated cellulose I materials in different forms such as sulphated cellulose whiskers, microcrystallites, nanocrystals or stable colloidal suspensions. Thus, the present invention provides a method for the concurrent production of crystalline, sulphated cellulose I and sulphated cellulose II materials from the H_2SO_4 hydrolysis of cellulose. The volume of the said aqueous
20 diluent is typically 0.2-5.0 times the volume of the said spent liquor, and more preferably, 0.5-3.0 times the volume of the said spent liquor. The volume of water to which the said diluted spent liquor is added to is typically 0.5-3.0 times the volume of the said diluted spent liquor.

According to the present invention, crystalline, sulphated cellulose II materials with
25 relatively low DP can also be produced by dissolution of cellulose in concentrated sulphuric acid ($>64\%$) at a known temperature for a known period of time, followed by dilution of the dissolved cellulose solutions with water, or by addition of the dissolved cellulose solutions to water over a known period of time at a given temperature (20-80°C).

30 The yield, the sulphate group content, the DP, and the morphological and other chemical properties of the said cellulose I and the said cellulose II materials isolated

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according to the present invention depend on the starting cellulose materials used, the conditions (e.g. time, temperature, H_2SO_4 concentration) of the hydrolysis of cellulose, the H_2SO_4 concentration and volume used for the dilution of the spent liquor, and the conditions for the treatment of the diluted spent liquor. For the concurrent production
5 of cellulose I and cellulose II materials, the hydrolysis is preferably performed at 56-68% H_2SO_4 at 40-65°C for 5-30 minutes. The dilution is preferably performed using 0-40% H_2SO_4 and the recrystallization of the soluble cellulose materials in the diluted spent liquor is preferably performed by slowly adding the spent liquor to water at 20-80°C or by heating it at 30-80°C for ≤ 48 h. FIG. 1 shows a flow diagram of the steps
10 involved in the isolation of crystalline, sulphated cellulose I and crystalline, sulphated cellulose II materials according to the current invention.

Cellulose in the present invention includes, but is not limited to cellulose from pulping and bleaching of lignocellulosic materials such as fully bleached Kraft pulp or sulfite pulp. It can also be, for example, bacterial cellulose, tunicate cellulose, or
15 microcrystalline cellulose.

Crystalline, sulphated cellulose I materials in the present invention include, but are not limited to, sulphated cellulose whiskers, microcrystallites and nanocrystals, nanocrystalline cellulose (NCC), and stable colloidal cellulose suspension.

Crystalline, sulphated cellulose II materials in the present invention are typically
20 soluble in more concentrated sulphuric acid solutions but are insoluble in water or in less concentrated sulphuric acid solutions.

An aqueous diluent in the present invention includes, but is not limited to 0-40% aqueous sulphuric acid (H_2SO_4).

The present invention is illustrated by, but not limited to, the following examples:

25 General Procedure A: Isolation of Crystalline, Sulphated Cellulose I and Diluted Spent Liquor from Sulphuric Acid Hydrolysis of Cellulose

A known amount of cellulose such as a fully-bleached kraft pulp is milled to pass through a 0.5-mm screen in a Wiley mill (Thomas-Wiley Lab mill, Model 4, Thomas Scientific, USA). A known volume of H_2SO_4 at a known concentration (56-68%) is

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heated to a desired temperature (40-65°C) and added to the milled cellulose under stirring with an impeller at 200 rpm. The mixture is heated at the desired temperature (40-65°C) for a known period of time (5-30 minutes) under stirring with an impeller at 500-600 rpm. At the end of heating, a known volume of deionized (DI) H₂O or H₂SO₄ (concentration ≤ 40%) is added under stirring with an impeller at 500-600 rpm. The suspension is centrifuged or allowed to settle over a known period of time. A known volume of the clear, top layer is decanted as the spent liquor.

All or a known portion of the remaining thick suspension is diluted with a known amount of cold (10°C) DI H₂O to give a residual H₂SO₄ concentration of 4-25% (residual H₂SO₄ concentration is calculated based on no H₂SO₄ consumption during hydrolysis), or is further hydrolyzed without or with the addition of a known amount of 0-72% sulphuric acid at a desired temperature (40-65°C) for a known period of time before dilution with a known amount of cold (10°C) DI H₂O to give a residual H₂SO₄ concentration of 4-25%. The suspension is centrifuged, or allowed to settle overnight and then centrifuged, or allowed to settle over a known period of time. Most of the clear, top layer is decanted off. The remaining thick suspension is washed twice by adding the same amount of DI H₂O as that which has been decanted, followed by mixing, centrifuging (or settling) and decanting of the top layer. After the final decanting, the thick white suspension is placed inside dialysis membrane tubes (or a dialysis module) and dialyzed against slow running tap water or DI H₂O for three days. After dialysis, the yield (yield of all the insoluble sulphated cellulose I) is determined by withdrawing and determining the oven-dried weight of a known amount of a small sample, and by taking into account whether all or only a portion of the thick suspension is used. A freeze-dried sample and an oven-dried sample are prepared. The sulphur (S) content of the freeze-dried sample is determined by titration after combustion according to a literature procedure [See reference by Soep and Demoen]. An X-ray diffractogram of the oven-dried sample is obtained on an X-ray diffractometer (Siemens, Bruker AXS D5000) using Co-K_α radiation. The degree of polymerization (DP) of the freeze-dried sample or the starting cellulose is, when needed, determined from the intrinsic viscosity $[\eta]$ in cm³/g measured according to SCAN-CM 15:99 test method by means of the formula, $DP^{0.905} = 0.75 [\eta]$. The formula is derived from the equation $[\eta] = 1.33 \times 10^{-4}$

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$M^{0.905}$ [See reference by Immergut et al.], where M is the molecular weight and $[\eta]$ is the intrinsic viscosity in 100 mL/g.

General Procedure B: Isolation of Crystalline, Sulphated Cellulose II from the Diluted Spent Liquor by Addition to Water

5 A known amount of the spent liquor is poured into a known amount of water or DI H₂O under manual mixing with a glass rod to give a residual H₂SO₄ concentration of, unless otherwise specified, 19.2% (calculated based on no H₂SO₄ consumption during the hydrolysis). Upon the addition of the spent liquor into the H₂O, a white precipitate is formed. The mixture of the white precipitate and the solution is centrifuged (or allowed
10 to settle), followed by decanting of a known volume of the clear top layer. A known volume (typically the same as the volume of top layer decanted) of DI H₂O is added, followed by mixing, centrifuging (or settling) and decanting of the top layer. The same washing procedure is repeated one more time. After the final decanting, the thick white suspension is placed inside dialysis membrane tubes (or a dialysis module) and
15 dialyzed against slow running tap water or DI H₂O for three days. After dialysis the suspension is freeze-dried to give the recrystallized sulphated cellulose II. The yield of the material is calculated based on the volume of the spent liquor decanted after hydrolysis, dilution and centrifugation. The sulphur (S) content of the freeze-dried material is determined by titration after combustion according to a literature procedure
20 [See reference by Soep and Demoen]. An oven-dried sample is prepared. X-ray diffractogram of the oven-dried sample is obtained on an X-ray diffractometer (Siemens, Bruker AXS D5000) using Co-K_α radiation. DP of the freeze-dried sample, when needed, is determined using the same method as that described in General Procedure A.

25 General Procedure C: Isolation of Crystalline, Sulphated Cellulose II from the Diluted Spent Liquor by Heating

A known amount of the diluted spent liquor is filtered and then heated at, unless otherwise specified, 45°C for 46 h. Upon heating, a white precipitate is formed. A known amount of the clear top layer (typically half of the total volume) is decanted off.
30 The remaining residue with the white precipitate is transferred into a dialysis

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membrane tube, and dialyzed against tap water or DI H₂O for 3 days. During dialysis the white precipitate settles down at the bottom of the membrane leaving a clear top layer. A known amount of the clear top layer (typically $\frac{3}{4}$ of the total volume) is decanted off and replaced with the same amount of DI H₂O. This displacement washing
5 is repeated two more times. After the final decanting, the remaining suspension is freeze-dried to give the recrystallized sulphated cellulose II. The yield of the material is calculated based on the volume of the spent liquor decanted after hydrolysis, dilution and centrifugation. Sulphur (S) content of the freeze-dried material is determined by titration after combustion according to a literature procedure [See reference by Soep
10 and Demoen]. An oven-dried sample is prepared. An X-ray diffractogram of the oven-dried sample is obtained on an X-ray diffractometer (Siemens, Bruker AXS D5000) using Co-K α radiation. The DP of the freeze-dried sample is, when needed, determined using the same method as that described in General Procedure A.

15 General Procedure D: Isolation of Crystalline, Sulphated Cellulose II from the Dissolved Solution of Cellulose in Sulphuric Acid

A known amount of cellulose such as a fully-bleached kraft pulp is milled to pass through a 0.5-mm screen in a Wiley mill (Thomas-Wiley Lab mill, Model 4, Thomas Scientific, USA). A known volume of H₂SO₄ at a known concentration (>64%) is added to the milled cellulose at room temperature (~23°C) under stirring with an
20 impeller at 200 rpm. The mixture is stirred with an impeller at 500-600 rpm for a known period of time (5-30 minutes) to give a clear, dissolved cellulose solution. A known volume of deionized (DI) H₂O is added to the cellulose solution under stirring with an impeller at 500-600 rpm, or the cellulose solution is added to a known volume of DI H₂O over a known period of time at a given temperature (20-80°C) to form a
25 white precipitate. The mixture of the white precipitate and the solution is centrifuged or allowed to settle. Most of the clear top layer (typically 80-90% of the total volume) is decanted off. The remaining thick white suspension is diluted with a known amount of DI H₂O, mixed and centrifuged (or allowed to settle), followed by decanting of the
30 the dilution. The same dilution, mixing, centrifuging (or settling) and decanting is repeated twice. After the final decanting, the thick white suspension is placed inside

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dialysis membrane tubes (or a dialysis module) and dialyzed against slow running tap water or DI H₂O for 3 days. After dialysis, the yield of the white precipitate/recrystallized material is determined by withdrawing and determining the oven-dried weight of a known amount of a small sample. A freeze-dried sample and an oven-dried sample are prepared. The sulphur (S) content of the freeze-dried sample is determined by titration after combustion according to a literature procedure [See reference by Soep and Demoen]. A X-ray diffractogram of the oven-dried sample is obtained on an X-ray diffractometer (Siemens, Bruker AXS D5000) using Co-K α radiation. DP of the freeze-dried sample is determined, when needed, using the same method as that described in General Procedure A.

EXAMPLE 1

29.2 g (oven-dried basis) of a fully-bleached, commercial softwood kraft pulp (DP = 972 ± 43) is milled and hydrolyzed, according to General Procedure A disclosed above, with 265 mL of 64% H₂SO₄ at 45°C for 10 minutes to give, after dilution with 545 mL of 40% H₂SO₄ (to give a residual H₂SO₄ concentration of 48%), centrifugation and decanting, 425 mL of a clear spent liquor and 350 mL of a thick suspension.

175 mL of the thick suspension is diluted with 1300 mL of cold DI H₂O to give a residual H₂SO₄ concentration of 5.7% and then processed according to General Procedure A disclosed above to give 7.04 g of the acid-insoluble material. The yield of the acid-insoluble material is determined to be 48.2% based on 350 mL of the thick suspension isolated. The S content of the acid-insoluble material is determined to be 0.95%. The DP of the acid-insoluble material is determined to be 68 ± 6 .

A portion (400 mL) of the spent liquor is poured into 600 mL DI H₂O to give a white precipitate according to General Procedure B disclosed above. The mixture of the white precipitate and the solution is processed, according to General Procedure B disclosed above and with the volume of the clear top layer decanted and that of DI H₂O used being 600 mL, to give 4.36 g of the recrystallized material. The yield of the recrystallized material is calculated to be 15.9% based on a decanted spent liquor of 425 mL. The S content of the material is determined to be 1.09%. The DP of the recrystallized material is determined to be 20 ± 2 .

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FIG. 2 shows X-ray diffractograms of the acid-insoluble material (— —) and the recrystallized material from the spent liquor. The X-ray diffractogram of the acid-insoluble material shows a diffraction pattern with 2θ (2 Theta) peaks of 17.8, 19.1 and 26.4° that are characteristic of cellulose I. The X-ray diffractogram of the recrystallized material shows a diffraction pattern with 2θ (2 Theta) peaks of 14.4, 23.4 and 25.7° that are characteristic of cellulose II.

EXAMPLE 2

29.1 g (oven-dried basis) of a fully-bleached, commercial softwood kraft pulp is milled and hydrolyzed, according to General Procedure A disclosed above, with 265 mL of 64% H_2SO_4 at 45°C for 25 minutes to give, after dilution with 635 mL of DI H_2O (to give a residual H_2SO_4 concentration of 18.8%), centrifugation and decanting, 400 mL of a clear spent liquor and 500 mL of a thick suspension.

The thick suspension is diluted with 500 mL of cold DI H_2O and then processed/washed according to General Procedure A disclosed above to give the acid-insoluble material. The yield of the material is determined to be 32.9%. The S content of the acid-insoluble material is determined to be 0.86%.

The spent liquor (400 mL) is filtered and then heated at 45°C for 46 h according to General Procedure C disclosed above. At the end of heating, 200 mL of the clear top layer is decanted off. The remaining residue with the white precipitate is transferred into a dialysis membrane, dialyzed and washed according to General Procedure C disclosed above with the volume of clear top layer decanted and that of the DI H_2O added being 150 mL. After the final decanting, 50 mL of the remaining suspension is freeze-dried to give 70 mg of the recrystallized material. The yield of the recrystallized material is calculated to be 0.24% based on a decanted spent liquor of 400 mL. The S content of the material is determined to be 0.70%.

FIG. 3 shows X-ray diffractograms of the acid-insoluble material (— —) and the recrystallized material from the spent liquor (—). The X-ray diffractogram of the acid-insoluble material has a diffraction pattern that is characteristic of cellulose I, while the X-ray diffractogram of the recrystallized material has a diffraction pattern that is characteristic of cellulose II.

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EXAMPLE 3

24.5 g (oven-dried basis) of a fully-bleached, commercial softwood kraft pulp (DP = 972 ± 43) is milled and hydrolyzed, according to General Procedure D disclosed above, with 250 mL of 72% H_2SO_4 at room temperature ($\sim 23^\circ\text{C}$) for 25 minutes to give a
5 clear, dissolved cellulose solution. The cellulose solution is diluted with 3L of cold (10°C) DI H_2O to produce white precipitate according to General Procedure D disclosed above. The mixture of the white precipitate and the solution is centrifuged. 2.75 L of the clear top layer is decanted off to give approximately 500 mL of a thick white suspension according to General Procedure D disclosed above. The white
10 suspension is diluted with 400 mL DI H_2O , mixed and centrifuged, followed by decanting of 400 mL of clear top layer. The same dilution, mixing, centrifuging and decanting is repeated twice, and the thick white suspension (500 mL) after the final decanting is dialyzed according to General Procedure D disclosed above. The yield of the white precipitate/recrystallized material is determined to be 73.6%. The S content
15 of the material is determined to be 1.18%. The DP of the recrystallized material is determined to be 43 ± 3 . FIG. 4 is the X-ray diffractogram of the recrystallized material and it shows a diffraction pattern that is characteristic of cellulose II.

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CLAIMS:

1. Crystalline, sulphuric acid soluble, sulphated cellulose II having a degree of polymerization $(DP) \leq 60$.
2. The crystalline, sulphated cellulose II of claim 1, recrystallized from solution.
- 5 3. A method for producing crystalline, sulphated cellulose II comprising:

diluting a spent liquor from the sulphuric acid hydrolysis of cellulose, with an aqueous diluent,

separating a diluted spent liquor from an acid-insoluble, sulphated cellulose I material, and

10 generating crystalline, sulphated cellulose II from the separated, diluted spent liquor.
4. The method according to claim 3, wherein the crystalline, sulphated cellulose II has a $(DP) \leq 60$.
5. The method according to claim 3 or 4, wherein the aqueous diluent is 0-40%
15 aqueous sulphuric acid.
6. The method according to any one of claims 3 to 5, wherein said generating comprises admixing the separated, diluted spent liquor with water.
7. The method according to any one of claims 3 to 5, wherein said generating comprises heating the separated, diluted spent liquor at 30 to 80 °C for up to 48 hours.
- 20 8. The method according to any one of claims 3 to 7, wherein said cellulose is a fully bleached Kraft pulp, sulfite pulp, bacterial cellulose, tunicate cellulose or microcrystalline cellulose.
9. The method according to any one of claims 3 to 7, wherein said cellulose is a fully bleached Kraft pulp.
- 25 10. The method according to any one of claims 3 to 7, wherein said cellulose is a sulfite pulp.

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11. The method according to any one of claims 3 to 7, wherein said spent liquor is from the sulphuric acid hydrolysis of cellulose of a fully bleached papermaking pulp with 56-68% sulphuric acid at 40-65 °C for 5-30 minutes.
12. A process for producing crystalline, sulphated cellulose materials comprising:
- 5 forming an acid-insoluble, sulphated cellulose material and a spent liquor from sulphuric acid hydrolysis of cellulose,
- diluting said spent liquor with an aqueous diluent,
- separating a diluted spent liquor from an acid-insoluble, sulphated cellulose material,
- 10 generating crystalline, sulphated cellulose II from the separated, diluted spent liquor, and
- generating crystalline, sulphated cellulose I from the separated, acid-insoluble, sulphated cellulose material.
13. A process according to claim 12, wherein said generating of crystalline, sulphated
- 15 cellulose I comprises isolating the separated, acid-insoluble, sulphated cellulose material to produce said crystalline, sulphated cellulose I.
14. A process according to claim 12, wherein said generating of crystalline, sulphated cellulose I comprises further hydrolysing the separated, acid-insoluble, sulphated cellulose material at a sulphuric acid concentration up to 68% and then isolating the
- 20 acid-insoluble, sulphated cellulose material to produce said crystalline, sulphated cellulose I.
15. The process according to claim 12, 13 or 14, wherein the aqueous diluent is 0-40% aqueous sulphuric acid.
16. The process according to any one of claims 12 to 15, wherein said generating of
- 25 crystalline, sulphated cellulose II comprises admixing the separated, diluted spent liquor with water.

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17. The process according to any one of claims 12 to 15, wherein said generating of crystalline, sulphated cellulose II comprises heating the separated, diluted spent liquor at 30 to 80 °C for up to 48 hours.

18. The process according to any one of claims 12 to 17, wherein said cellulose is a
5 fully bleached Kraft pulp, sulfite pulp, bacterial cellulose, tunicate cellulose or microcrystalline cellulose.

19. The process according to any one of claims 12 to 17, wherein said cellulose is a fully bleached Kraft pulp.

20. The method according to any one of claims 12 to 17, wherein said cellulose is a
10 sulfite pulp.

21. The method according to any one of claims 12 to 17, wherein said spent liquor is from the sulphuric acid hydrolysis of cellulose of a fully bleached papermaking pulp with 56-68% sulphuric acid at 40-65 °C for 5-30 minutes.

22. A process for producing crystalline, sulphuric acid soluble, sulphated cellulose II
15 having a degree of polymerization (DP) ≤ 60 , comprising:

dissolution of cellulose in concentrated sulphuric acid to form a solution of dissolved cellulose material comprising sulphated cellulose material, and

generating crystalline, sulphated cellulose II from said solution by dilution of said solution with an aqueous diluent.

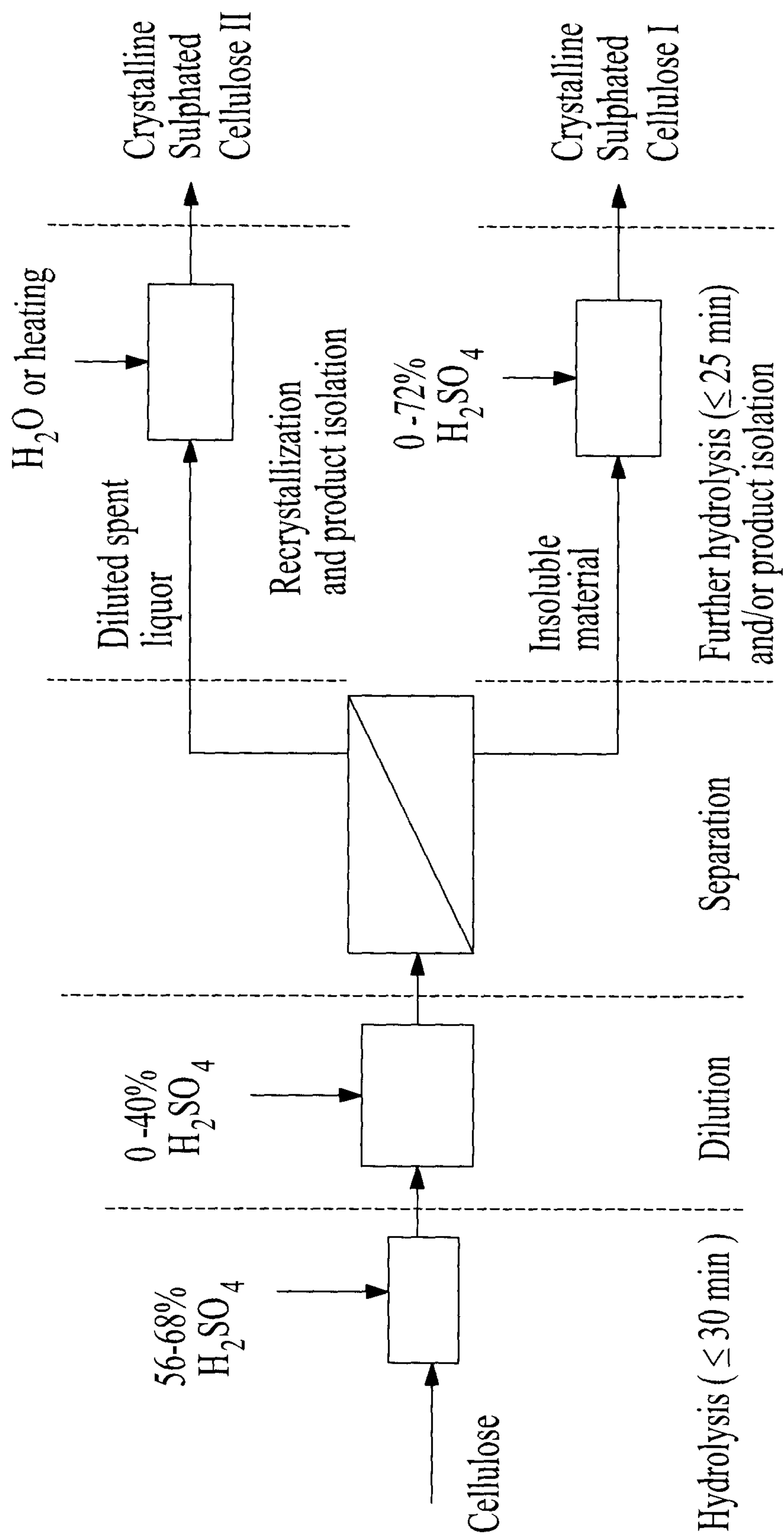
20 23. The process according to claim 22, wherein said cellulose is a fully bleached Kraft pulp, sulfite pulp, bacterial cellulose, tunicate cellulose or microcrystalline cellulose.

24. The process according to claim 22, wherein said cellulose is a fully bleached Kraft pulp.

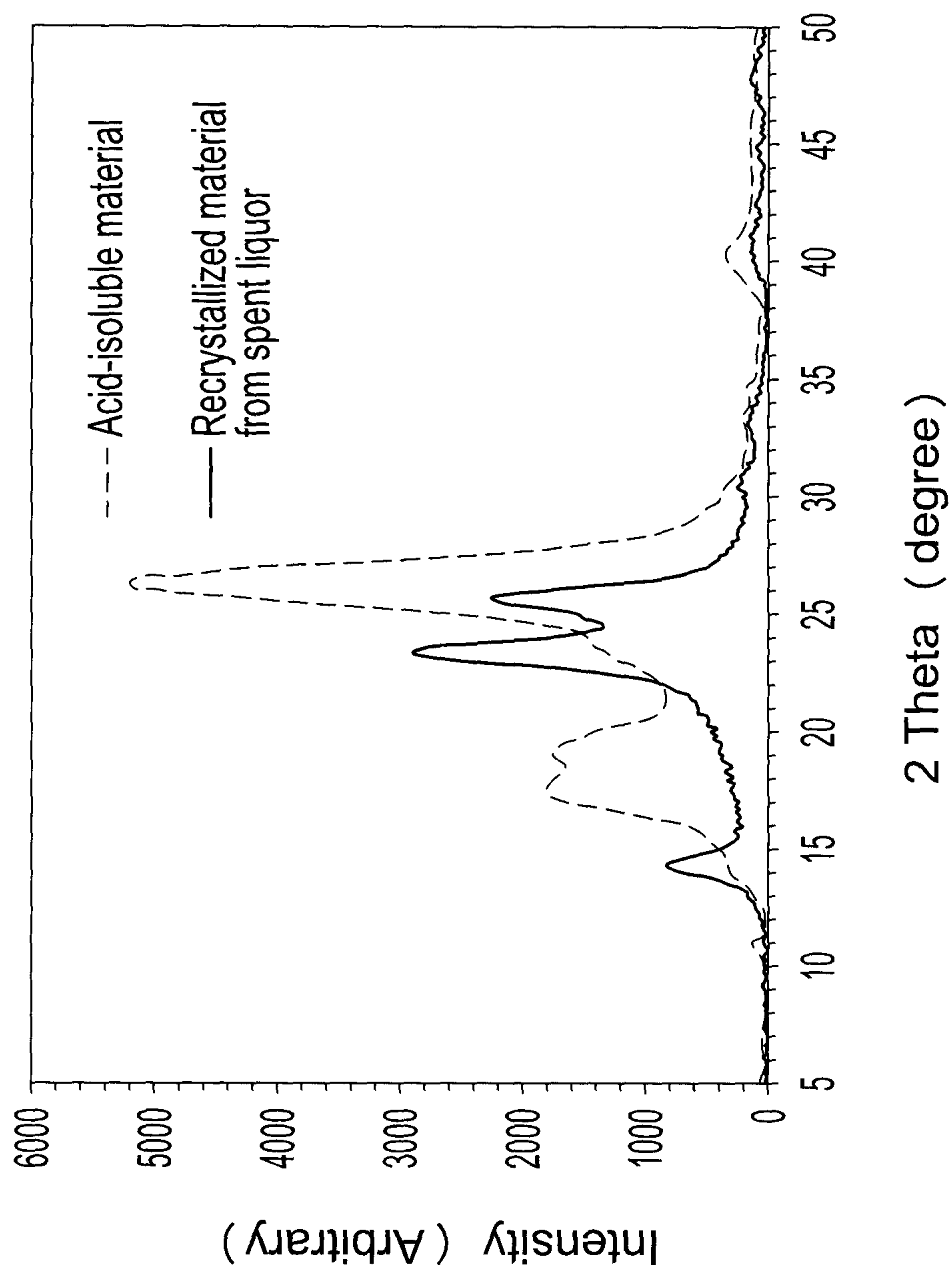
25. The process according to claim 22, wherein said cellulose is a sulfite pulp.

25 26. The process according to claim 22, wherein said spent liquor is from the sulphuric acid hydrolysis of cellulose of a fully bleached papermaking pulp with 56-68% sulphuric acid at 40-65 °C for 5-30 minutes.

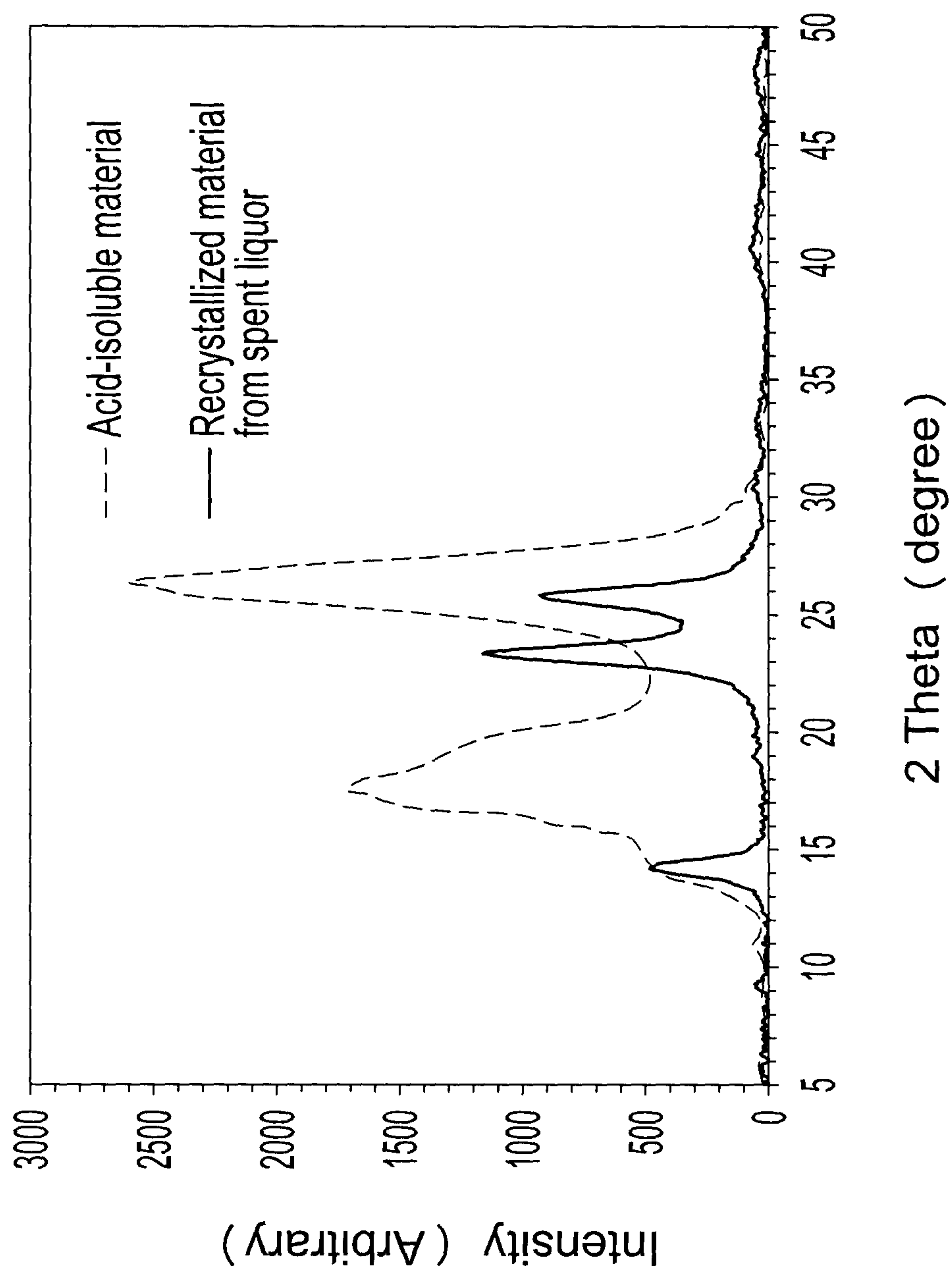
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Fig-1

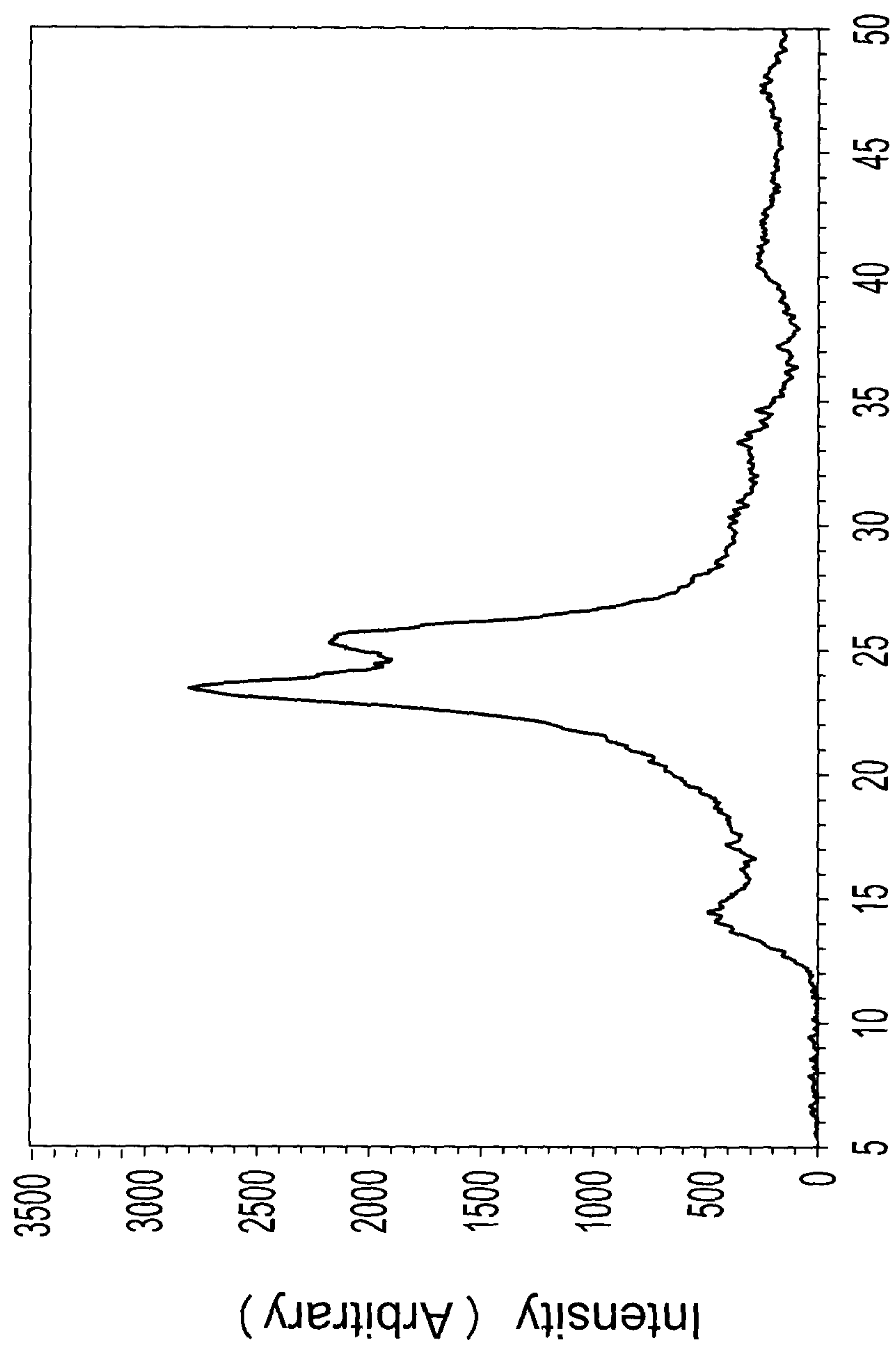
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**Fig-2**

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Fig. 3

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2 Theta (degree)

Fig. 4