



(51) International Patent Classification:

D21C 1/04 (2006.01) **D21C 3/00** (2006.01)
B29C 70/06 (2006.01) **D21C 5/00** (2006.01)

(21) International Application Number:

PCT/CA2014/000076

(22) International Filing Date:

27 January 2014 (27.01.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2,803,863 25 January 2013 (25.01.2013) CA

(71) **Applicant:** VENTIX ENVIRONNEMENT INC.
[CA/CA]; Suite 407, 2550, Chemin Bates, Montreal,
Québec H3S 1A7 (CA).

(72) **Inventor:** ESSADDAM, Hatem; Apt. 30, 2865, rue de la
Renaissance, Boisbriand, Québec J7H 1T9 (CA).

(74) **Agent:** FASKEN MARTINEAU DUMOULIN LLP;
800, Square Victoria, Stock Exchange Tower, P.O. Box
242, Suite 3700, Montreal, Québec H4Z 1E9 (CA).

(81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) **Title:** PROCESS FOR ISOLATING CELLULOSE FROM CELLULOSIC BIOMASS, ISOLATED CELLULOSE OF TYPE I AND COMPOSITE MATERIALS COMPRISING SAME

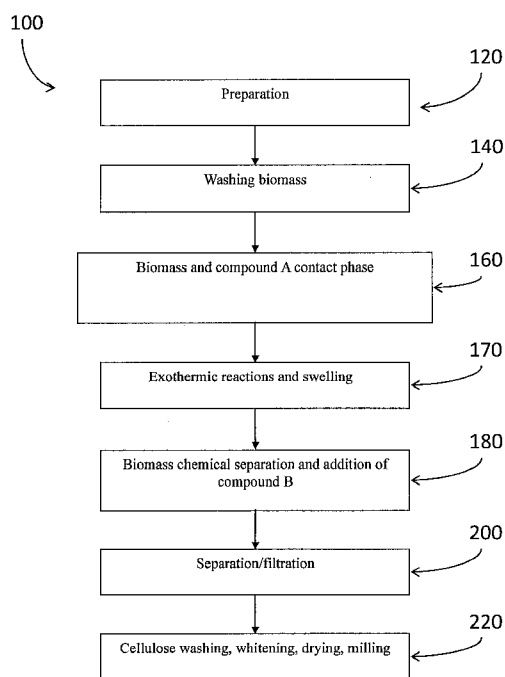


FIGURE 1

(57) **Abstract:** Described herein are processes for the production of a cellulose pulp and processes for isolating cellulose from cellulose-containing biomass. The processes of the invention comprises contacting the biomass with a source of anions and a source of cations, the source of anions and the source of cations being selected to react exothermically with the biomass and with each other. The processes of the invention have the particularity of generating exothermic reactions through enthalpies of reaction and mixture. Accordingly, the processes of the invention do not require any supply of external energy since the required energy is provided by chemical reagents that are already present in the biomass or added as needed. The invention also relates to isolated cellulose obtained from these processes and the use of same in various materials.

**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report (Art. 21(3))*

**PROCESSES FOR ISOLATING CELLULOSE FROM CELLULOSIC BIOMASS,
ISOLATED CELLULOSE OF TYPE I AND COMPOSITE MATERIALS
COMPRISING SAME**

RELATED APPLICATION

- 5 The present application claims priority to Canadian patent application No. 2,803,863 filed January 25th, 2013, the content of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

- 10 The present invention relates to the field of biomass delignification and cellulose extraction. More particularly, the invention relates to processes for the production of a cellulose pulp and processes for isolating cellulose from cellulose-containing biomass. The invention further relates to isolated cellulose obtained from these processes and to the use of same in various materials.

BACKGROUND OF THE INVENTION

- 15 Plant biomass is primarily composed of cellulose (~50%), lignin (~ 25%) and hemicelluloses (~ 25%).

- Although cellulose was first extracted using mechanical processes, nowadays cellulose is mostly obtained by chemical extraction processes, that were first developed on an industrial scale in Europe in 1850's. Those chemical processes
20 generally yield between 80 and 96% of cellulose pulp, some lignin remaining with the cellulose. Lignin is generally undesirable because of its adverse effect on paper, in particular as regards to its resistance and yellowing over time.

- Conventional chemical processes such as sulfite, bisulfite (acid) and Kraft or sulphate (alkaline) processes, have been designed to remove most lignin from
25 cellulose as well as extractives and hemicelluloses. Chemical pulp is generally produced within large reactors at elevated temperatures (from 100°C to 180°C) and at high pressures (5 to 7,5 bars). Biomass is usually pressure-cooked in the presence of chemical compounds for 15 to 25 hours. Cellulose fibres are then washed, rinsed, cleaned and bleached.

- 30 Sulfite and bisulfite chemical processes are used mainly on softwood. Both processes are based on wood chips' lignin dissolution in sulfuric acid salts, either

sulfites (SO_3^{2-}) or bisulfite (HSO_3^-) depending on the pH. Both processes take place in wide pressurized reactors. Counterions used are sodium (Na^+), calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}) or ammonium (NH_4^+).

5 The commonly used sulfate or Kraft process has the advantage of treating a great variety of plants such as hardwood and softwood, sugar cane and reed, just to name a few. The Kraft process requires high heat and high pressure for several hours. The pulp obtained is dark in appearance and, for quality papers requiring a high degree of whiteness; the pulp must undergo chemical bleaching. Both processes are highly
10 polluting despite efforts since the 1930's to recover the chemical products used therein.

Chemical processes have been periodically improved since their first discovery but they still remain quite similar to the original processes. Almost all processes tend to denature cellulose and lignin fibres due to exposure to high pressures and high temperatures and also due to the use of salts and counterions that change both the
15 chemical and physical structure of molecules. Chemical processes further require massive industrial facilities and huge investments to build and operate since these known processes require large amounts of energy and water and they must also deal with air and water pollutants.

Other processes have been developed to overcome some of these disadvantages by
20 using a combination of simple and somehow soft chemical reagents and high physical constraints (temperature and pressure) for the removal of lignin and for obtaining a cellulosic material with varying degrees of purity. Examples of these known processes include steam explosion delignification or Iotech process, Organosolv process and CIMV process (see for instance US patent No 1,655,618,
25 US patent No 4,645,541, European patent applications EP 0503304 and EP 0584675 and International PCT publication Nos. WO 2010/071805, WO 2009/092749 and WO 2012/000093). All of these processes require however expensive equipment because of their use of high temperatures (between 95 °C and 270 °C) and pressure (between 3 and 40 bars). In addition, these processes do not handle large volumes
30 of material for industrial production, precisely because of the high cost of their facilities.

US Patent No 6824599 and International PCT publication WO 2005/017001 disclose a method using ionic liquids for obtaining cellulose. According to the method described, the biomass is immersed in ionic liquids and it is subjected to microwave

radiation (source of energy) and to pressure conditions of several atmospheres. Although the method provides some advantages over the Kraft process, it still presents some disadvantages, including the need for thermal energy and the use of high pressure and the low yield of pure cellulose.

- 5 Accordingly, there is a need for new chemical processes for the delignification of biomass and extraction of cellulose. There is more particularly a need for a process which can be carried out at ambient pressure and which can generate their its energy such that no external source of energy such as heating is required. There is also a need for pulp preparation and cellulose extraction processes that can be
- 10 implemented in variable sizes, such as large industrial facilities or smaller mobile units installed near or on the very sites of wood processing activities, and still be relatively inexpensive and commercially viable. There is also a need for more environmental friendly processes that requires less water and that produce less water and gas pollutants. There is also a need for a cellulose that is more reactive
- 15 and that has desirable purity, chemical and mechanical characteristics.

The present invention addresses these needs and other needs as it will be apparent from review of the disclosure, drawings and description of the features of the invention hereinafter.

SUMMARY OF THE INVENTION

- 20 The invention relates to delignification of biomass and extraction cellulose from cellulosic biomass.

One particular aspect of the present invention concerns aprocess for the production of a cellulose pulp, comprising:

- providing a biomass comprising cellulose, hemicelluloses and lignin;
- 25 – contacting the biomass with a source of anions and a source of cations, wherein said source of anions and said source of cations are selected to react exothermically with the biomass and with each other;
- allowing exothermic reactions under conditions and for a period of time sufficient to break intermolecular bonds existing between lignin,
- 30 cellulose and hemicelluloses;
- obtaining a cellulose pulp comprising solubilised hemicelluloses and solubilised lignin.

In one embodiment, the biomass provides at least a portion of said source of anions A.

A related aspect of the invention concerns process for the production of a cellulose pulp, comprising:

- 5 - providing a biomass comprising cellulose, hemicelluloses and lignin;
- providing a source of anions A and a source of cations B, wherein said source of anions A and said source of cations B are anionic precursors of an ionic liquid of formula AB, and wherein said source of anions A and source of cations B are selected to react exothermically with the
- 10 biomass and with each other;
- contacting the biomass with the source of anions A and with the source of cations B, wherein said contacting is carried out under conditions and for a period of time allowing the formation of said ionic liquid AB, and wherein said contacting is exothermic and breaks intermolecular bonds
- 15 existing between lignin, cellulose and hemicelluloses;
- obtaining a cellulose pulp comprising i) a solid phase composed principally of cellulose and ii) a heterogeneous viscous mixture comprising solubilised hemicelluloses and solubilised lignin.

Another aspect of the invention concerns a process for isolating cellulose from

20 biomass, comprising :

- a) providing a biomass comprising cellulose, hemicelluloses and lignin;
- b) contacting the biomass with a compound A for impregnating at least partially said biomass and for obtaining an impregnated acidic biomass, wherein compound A is a source of anions and wherein
- 25 compound A reacts exothermically with the biomass;
- c) contacting the impregnated acidic biomass with a compound B, wherein compound B is a source of cations and wherein compound B reacts exothermically with compound A impregnated within the acidic biomass;
- 30 d) allowing exothermic reactions under conditions and for a period of time sufficient to break intermolecular bonds existing between lignin, cellulose and hemicelluloses and produce a cellulose pulp comprising solubilised hemicelluloses and solubilised lignin;
- e) isolating cellulose from said pulp.

35

Another aspect of the invention concerns isolated cellulose obtained according to the processes described herein.

Particularly, the invention relates to an isolated cellulose characterized by a FTIR spectrum that is distinguishable from the FTIR spectrum for cellulose type II. In one particular embodiment, the FTIR spectrum of said isolated cellulose is characterized by a peak at 1730 cm^{-1} .

The invention relates also to an isolated cellulose characterized by a X-ray spectrum distinguishable from the X-ray spectrum for cellulose type II. In one particular embodiment, the X-ray spectrum of said cellulose comprises a peak at $2\theta = 15,0$ (1-10), a peak at $2\theta = 16,6$ (110), a peak at $2\theta = 22,7$ (200) and a peak at $2\theta = 34,5$ (004). In another embodiment, the X-ray spectrum of said cellulose comprises two peaks at $2\theta = 29,9$ and $2\theta = 38,3$.

A further aspect of the invention concerns a composite material comprising a resin and/or a hardener mixed with an isolated cellulose as defined herein.

A further aspect of the invention concerns a composite material having distinctive characteristics, such as an improved elasticity and/or incorporating at 15 % w/w of cellulose.

An advantage of the present invention is that it provides relatively simpler, cheaper and more efficient means than all other chemical processes for making cellulose pulp and extracting cellulose from biomass. The processes of the invention can be implemented in variable sizes, such as large industrial facilities or smaller mobile units installed near or on the very sites of wood processing activities. The processes of the invention can be carried out at ambient pressure conditions and do not require external source of energy such as heating, pressurizing or the like. The chemical processes of the invention are likely more environmental friendly because they use less water and they produce less water and gas pollutants than other existing chemical processes. Furthermore, the cellulose that is obtained from these processes possess advantages in terms of purity (i.e. less lignin and less hemicelluloses), cell integrity, reactivity and abundance, than typical commercial type I and type II celluloses.

Additional aspects, advantages and features of the present invention will become more apparent upon reading of the following non-restrictive description of preferred

embodiments which are exemplary and should not be interpreted as limiting the scope of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow diagram showing a process for cellulose extraction, according to one embodiment of the invention.

Figures 2A and 2B are schematic drawings illustrating the process of **Figure 1**, **Figure 2A** illustrating steps 160, 170 and 180 and **Figure 2B** steps 200 and 220 of the process of **Figure 1**. The following numbers represent the illustrated elements: (1) Compound A; (2) Biomass; (3) Biomass swelling; (4) Compound B; (5) Heating; (6) Gas emission; (7) Solid substance; (8) heterogeneous viscous mixture; (9) Filter; (10) Filtrate; (11) Washing; (12) Cellulose; (13) Filter; (14) Ventilation; (15) Blending; (16) Sieving; and (17) Cellulose powder.

Figure 3 is a bar graph depicting breakdown analysis of hemicelluloses, lignin and cellulose obtained according to Examples 1 to 4.

Figures 4A-4C are curves depicting infrared spectrum (IR) of the [$< 20 \mu\text{m}$] sieved fraction of the cellulose obtained from white birch wood chips according to one embodiment of the invention (Invention, Type I; **Fig. 4A**), commercial cellulose Alpha from Sigma Aldrich (Type II, **Figure 4B**) and an overlap of both curves (**Figure 4C**).

Figures 5A-5D are RX diffractograms curves of various celluloses. **Figure 5A**: Avicel PH101 Type I cellulose (Park et al. 2010. Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulose performance. Biotechnol Biofuels. 2010; 3: 10) **Figure 5B**: Type II cellulose (Biganska O., 2002. Étude physico-chimique des solutions de cellulose dans la N-méthylmorpholine-N-oxyde. Thesis, École des Mines, Paris, 133p.). **Figure 5C**: [$20\mu\text{m}$, $45\mu\text{m}$] sieved fraction of cellulose obtained from white birch wood chips according to one embodiment of the invention; **Figure 5D**: overlap of the curves of **Figure 5A** and **Figure 5C**.

Figures 6A-6D are pictures of microscopic imaging from scanning electron microscopy (SEM). The [$< 45 \mu\text{m}$] sieved fraction of the cellulose obtained from maple wood chips according to one embodiment of the invention, at a $200 \mu\text{m}$ scale (**Figure 6A**) and $20 \mu\text{m}$ scale (**Figure 6B**). Avicel PH101 Type I cellulose at a $300 \mu\text{m}$ scale (**Figure 6C**) and $60 \mu\text{m}$ scale (**Figure 6D**) (Ribet J., 2003.

Fonctionnalisation des excipients: application à la comprimabilité des celluloses et des saccharoses, Thesis, Université Limoges, France, 263p.).

5 **Figures 7A and 7B** are respectively length and width bar graphs (in μm) depicting size distribution of the [$< 45 \mu\text{m}$] sieved fraction of the cellulose obtained from maple wood chips according to one embodiment of the invention.

Figure 7C is a bar graph depicting a size distribution of cellulose fibers length pictured in Figure 6C (Avicel PH101 Type I cellulose).

10 **Figure 8** depicts curves of polymerization for [$< 20 \mu\text{m}$] and [$20\mu\text{m}, 45\mu\text{m}$] sieved fractions of the cellulose obtained from white birch wood chips according to one embodiment of the invention, and for a commercial type I cellulose (Avicel PH101, FMC Biopolymer) compared to Epolam 2015™.

Figure 9A depicts thermogravimetric analysis curves (TGA) for the [$< 45 \mu\text{m}$] sieved fraction of the cellulose obtained from maple wood chips according to one embodiment of the invention.

15 **Figure 9B** depicts dynamic mechanical analysis curves (DMA) for the [$< 45 \mu\text{m}$] sieved fraction of the cellulose obtained from maple wood chips according to one embodiment of the invention. The curves for Sample 1 refers to resin epoxy Epon 862™ + 10% cellulose, and the curves for sample 2 refers to pure epoxy Epon 862™.

20 **Figure 10** is a picture of microscopic imaging of a nanoparticle (size smaller than $1 \mu\text{m}$) of cellulose obtained from white birch wood chips according to one embodiment of the invention.

Figure 11A displays a curve depicting a FTIR spectrum of non-oxidized isolated cellulose (DS close to 0).

25 **Figure 11B** displays a curve depicting a FTIR spectrum of oxidized cellulose (DS = 3).

Figure 11C displays an overlap of the curves of Figure 11A and 11B.

DETAILED DESCRIPTION OF THE INVENTION

A) General overview of the invention

The present invention is concerned with the production of a cellulose pulp and with processes for isolating cellulose from cellulose-containing biomass. Contrary to
5 known chemical processes which require large amount of energy (e.g. high heat and high pressure), the processes of the invention have the particularity of generating exothermic reactions through enthalpies of reaction and mixture. Accordingly, the processes of the invention do not require any external energy supply to modulate the temperature, and/or the pressure since the required energy is provided by chemical
10 reagents that are already present in the biomass or added as needed.

The essence of the invention relies on the use of two main compounds A and B reacting with the biomass. Chosen compounds are acting both as reagents and as sources of anions and cations for the making of a solution and eventually an ionic liquid which will solubilise lignin and hemicelluloses and strip both components from
15 cellulose. When properly selected, dosed and/or mixed, compounds A and B will react with the biomass to generate sufficient energy through enthalpies of reactions and enthalpies of mixture to break intermolecular bonds existing between cellulose, lignin, and hemicelluloses and will allow a solubilisation of the lignin and hemicelluloses.

20 The processes of the invention do not require addition of water and they require fewer chemical products than known chemical processes and these chemicals may be recycled totally or partially. Moreover, cellulose fibres obtained according to the invention are depleted from most of the original lignin and these cellulose fibers can conserve native molecular properties or they can be modified chemically according to
25 selected operating conditions.

B) Definitions

For the purpose of the present invention, the following terms are defined below.

As used herein and in the appended claims, the singular forms "a", "an", and "the" include plural referents unless the context clearly indicates otherwise. Thus, for
30 example, reference to "a compound" includes one or more of such compounds and reference to "the process" includes reference to equivalent steps and processes or

methods known to those of ordinary skill in the art that could be modified or substituted for the methods described herein.

As used herein the term "**biomass**" refers to cellulose-containing products such as wood, plant biomass and derivatives including, but not limited to, hard and softwood
5 including trunk, bark, branches, roots and leaves, plants and herbs, hemp, straw, vegetable waste, wood residues, woodchips, algae, papers, cardboards and the like.

"**Ionic liquid**" as used herein refers to liquid salts which possess high thermal stabilities and are liquid around room temperature (typically -100°C to 200°C, but this might even exceed 300°C) (Wasserman, P., Welton. T., 2003, Ionic Liquids in
10 Synthesis, Wiley-VCH, p. 1-6, 41-55 and 68-81). Ionic liquids are largely made of ions and short-lived ion pairs, mostly an organic cation combined with an organic or inorganic anion. There are over a million possible cation-anion combinations and new combinations are emerging constantly. For instance, ionic liquid may be a quaternary ammonium or a quaternary phosphoniums, where the cations bear amine
15 groups; ethers or alcohols; acids or esters; thiols; vinyl; allyl; alkynes; nitriles or even chiral cations. The ionic liquid may be a compound in which an organic or inorganic anions is selected among chirals functionalized by nitriles, hydroxyborates, Lewis bases, metal salts or heteropolyanions. Particular examples of ionic liquids according to the invention include, but are not limited to those described in Patent Nos US
20 5683832 A, US 5827602 A, EP 2162435 and EP 2295440. These substances are variously called room temperature ionic liquids (RTIL), liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, ionic glasses.

As used herein, the term "**cellulose**" includes an organic oligomer or homopolymer ($C_6H_{10}O_5$)_n consisting of a linear chain of several β(1→4) linked D-glucose units with,
25 at the end of each chain, both a reducing group and a non-reducing group. Cellulose is the most abundant organic polymer on earth. The term "cellulose" encompasses all different form of cellulosic material including, but not limited to, sheets, fibers, fibrils, strands, microcrystalline cellulose (MCC), nanocrystalline cellulose (NCC) and the like. As used herein, the term "**isolated cellulose**" refers to cellulose obtained,
30 extracted, purified, etc. from cellulose-containing biomass, preferably by using a process according to the present invention.

As used herein, the terms "**type I cellulose**" or "**cellulose of type I**" or "**cellulose I**" or "**native cellulose**" refers to cellulose in which all the cellulose strands are parallel and have no inter-sheet hydrogen bonding. Cellulose I contains two coexisting phase

cellulose I_α (triclinic) and cellulose I_β (monoclinic) in varying proportions dependent on its origin: I_α being found more in algae and bacteria whilst I_β is the major form of higher plants (Atalla RH. 1999. The individual structures of native celluloses. Proceedings of the 10th International Symposium on Wood and Pulping Chemistry, Main Symposium; Yokohama, Japan. 07-10 June 1999; pp.608-614). Cellulose I_α and cellulose I_β can be found in mixed proportion in all sources (J. Am. Chem. Soc. 9 vol. 125, no. 47, 2003 14300-14306; J. Am. Chem. Soc. 9 vol. 124, no. 31, 2002 9074-9082).

As used herein, the terms "**type II cellulose**" or "**cellulose of type ii**" or "**cellulose II**" refers to cellulose that is generally monoclinic and thermodynamically more stable than cellulose I. The structure of cellulose II shows an antiparallel arrangement of the strands and it has both intra- and inter- sheet hydrogen-bonding. Cellulose II can be obtained by mercerization of cellulose I for example. It is generally generated after chemical (i.e. mercerization) or chemico-mechanical treatment of lingocellulosic biomass.

As used herein, the term "**cellulose pulp**" refers to a viscous or semi-liquid mixture deriving from chemical treatment of cellulose-containing biomass, and comprising fibrous cellulose material, solubilised hemicelluloses, solubilised lignin and other residues or components deriving from the biomass or the chemical-treatment.

As used herein, the term "**enthalpy of reaction**" refers to an energy change of a reaction ΔH . It is the amount of energy or heat absorbed in a reaction. If the energy is required, ΔH is positive, and if energy is released, ΔH is negative.

As used herein, the term "**enthalpy of mixture**" refers to the energy that is taken up or released upon mixing of two chemical substances. When the enthalpy of mixing is positive, mixing is endothermic while negative enthalpy of mixing signifies exothermic mixing. Accordingly, as used herein, the term "**reacts exothermically**" refers to a chemical reaction in which heat and somehow pressure is released upon mixing of two or more chemical substances (e.g. biomass and compound A and/or B, compounds A+B, etc.).

30

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS**Process for biomass delignification and cellulose extraction**

One particular aspect of the present invention relates to a process for the production of a cellulose pulp. The pulp may then be washed, dried, grinded and/or milled to
5 yield native or modified cellulose depending on operating conditions.

In one embodiment the process for the production of a cellulose pulp comprises:

- providing a biomass comprising cellulose, hemicelluloses and lignin;
- contacting the biomass with a source of anions and a source of cations,
10 wherein the source of anions and the source of cations are selected to
react exothermically with the biomass and with each other;
- allowing exothermic reactions under conditions and for a period of time
sufficient to break intermolecular bonds existing between lignin, cellulose
and hemicelluloses;
- obtaining a cellulose pulp comprising solubilised hemicelluloses and
15 solubilised lignin.

In another embodiment the process for the production of a cellulose pulp comprises:

- providing a biomass comprising cellulose, hemicelluloses and lignin;
- providing a source of anions A and a source of cations B, wherein the
20 source of anions A and the source of cations B are anionic precursors of
an ionic liquid of formula AB, and wherein the source of anions A and the
source of cations B are selected to react exothermically with the biomass
and with each other;
- contacting the biomass with the source of anions A and with the source of
cations B, wherein the contacting is carried out under conditions and for a
25 period of time potentially allowing the formation of the ionic liquid AB, and
wherein the contacting is exothermic and breaks intermolecular bonds
existing between lignin, cellulose and hemicelluloses;
- obtaining a cellulose pulp comprising i) a solid phase composed principally
of cellulose and ii) a heterogeneous viscous mixture comprising
30 solubilised hemicelluloses and solubilised lignin and other residues from
the reaction.

Another particular aspect of the invention concerns a process for isolating cellulose from biomass. According to one embodiment the process comprises:

- a) providing a biomass comprising cellulose, hemicelluloses and lignin;
- b) contacting the biomass with a compound A for impregnating at least partially the biomass and for obtaining an impregnated acidic biomass, wherein compound A is a source of anions and wherein compound A reacts exothermically with the biomass;
- c) contacting the impregnated acidic biomass with a compound B, wherein compound B is a source of cations and wherein compound B reacts exothermically with compound A impregnated within the acidic biomass;
- d) allowing exothermic reactions under conditions and for a period of time sufficient to break intermolecular bonds existing between lignin, cellulose and hemicelluloses and produce a cellulose pulp comprising solubilised hemicelluloses and solubilised lignin;
- e) isolating cellulose from said pulp.

- 15 According to particular embodiments, the invention may allow the extraction of native and/or modified cellulose or functionalized and/or non-functionalized cellulose, either by partial or total removal of lignin and hemicelluloses.

According to the principles of the invention, using, adding and/or contacting anions (compound A) and cations (compound B) to the biomass results in exothermic reactions generated by enthalpy of reaction and enthalpy of mixture which lead to the dissolution of the lignin and hemicelluloses components and the production of a cellulose pulp. No other external energy supply is therefore needed for the reaction to occur. A person skilled in the art will understand that numerous pairs of compounds A and B may be used to generate ionic liquids, and that each particular pair can be selected for its own characteristics and desired activity when used in the process.

According to the present invention, the source of anions (compound A) is defined as any compound containing a proton in the sense of the Lowry-Bronsted theory and may become an anionic precursor in an ionic liquid. Compound A is then defined as being an anionic precursor of an ionic liquid in the sense that this compound becomes an anionic source when mixed with a cationic source being compound B, in this case. Compound A may be a liquid, a solid or a gas.

Compound A may contain the same type of anionic precursor or different types. Compound A may then be defined as $A_1A_2...A_i$, index i characterizing the number of different anionic precursors, including all forms comprised in the predominance pH

diagram (i.e. compound A can be a salt or an acid). When compound A is gaseous (hydrochloric acid, for example) or solid (p-toluensulfonic acid, for example), one can solubilise the gas or solid in a solvent prior to contacting with the biomass, in order to improve the reactivity of compound A and optimize the processes of the invention.

- 5 According to the present invention, the source of cations (compound B) is a compound that may be selected from: primary amines, secondary amines, tertiary amines or polyamines or phosphines or polyphosphines molecules, quaternary ammonium or quaternary phosphoniums, ethers or alcohols, acids or esters, thiols, vinyl, allyl, alkynes, nitriles or chiral cations, chirals functionalized by nitriles, hydroxyborates, Lewis bases, metal salts or heteropolyanions. According to the invention, Compound B is a cationic source when reacting with compound A (anionic source) to produce solution AB or an ionic liquid.

- Compound B may contain the same type of cationic precursor or different types. Compound B may then be defined as $B_1B_2...B_j$, index j characterizing the number of different cationic precursors including all forms comprised in the predominance pH diagram (i.e. compound B can be a salt or base). In one particular implementation, indexes i and j can be equal or different. Compound B is preferably a liquid, but it can also be solid or gaseous. Particular examples of compound B include, but is not limited to, 2-Aminoethanol, 2,2'-Iminodiethanol and 2,2',2-nitrilotriethanol. In preferred embodiments, compound B is 2-Aminoethanol or 2,2'-Iminodiethanol.

- A person versed in the art will understand that A and B work together and are selected to form a couple AB having an enthalpy of mixture that is sufficient to modify the structure of the biomass without reaching overly high temperature that would partially or totally denature or burn the lignin, the hemicelluloses and/or the cellulose. In the case where enthalpies are too strong, it is possible to artificially cool the reaction in order to prevent denaturing or burning either chemically (i.e. by adding a neutral solvent such as ethanol or cold water) or physically (i.e. by cooling the reactor).

- Typically, the anions (compound A) and cations (compound B) are added separately and in two different phases. In particular embodiments, compound A is added in a first phase before compound B, while in other embodiments compound B is added in a first phase and then, compound A is added in second phase. In particular embodiments, a certain period of time is allowed between the two phases (i.e. minimum contacting time before adding the second compound to mixture comprising

the first compound). That period of time may be only a few seconds or a few minutes (e.g about 15 sec, about 30 sec, about 45 sec, about 1 min, about 2 min, about 5 min, about 10 min, about 15 min, about 30 min or more) or it may be longer (at least 15 min, at least 30 min, at least 45 min, at least 1h, at least 2h or more). Those skilled in the art understand that the time may vary according to various factors and conditions, including but not limited to the type and condition of the biomass being used as the starting material, the identity and amount of compound A and/or B, etc.

Alternatively, compounds A and B can be carried out by the same molecule where a change in pH, corresponding to the field dominance, would predominantly generate compound A or compound B. The addition of A and B becomes then predominant if one chooses to put the two compounds in that order. Accordingly the source of anions and the source of cations may be a single zwitterion or a zwitterionic compound. Accordingly, the invention envisions the use of zwitterions in combination with or replacement to either or both components A and B. The zwitterion may be selected from and not limited to amino acids (e.g. histidine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, valine, arginine, asparagine, aspartic acid, cysteine, glutamic acid, glutamine, glycine, ornithine, proline, glycine, alanine, isoleucine, cystine, selenocysteine, serine, tyrosine), arsenobetaine, betaine, bicine, ceftazidime, cephaloridine, edelfosine, ilsoionic point, miltefosine, perifosine, quinonoid zwitterion, tricine, and trimethylglycine.

Alternatively, the source of anions/cations may already be present in the biomass. In such case the compound A or B could be omitted from the reaction. For instance, some components may already be present in the biomass such as in the bark of some trees (e.g. betulinol, lupeol, oleanolic acid, betulinic acid and the like, comprised in white birch bark).

Without being bound by any theory, the impregnation of the biomass with compound A or B may cause a swelling or increase in volume of the biomass causing a rupture of hydrogen and Van der Waals bonds due to space occupation of one or more external molecules. In addition, the exothermic reactions occurring during the processes of the invention will weaken and eventually break the intermolecular bonds existing between lignin, cellulose and hemicelluloses to produce a cellulose pulp comprising solubilised hemicelluloses and solubilised lignin. It is hypothesised that compound B (or A, if A is added first) reacts with compound A (or with B if A is added first) within the impregnated biomass and that it will modify

chemically lignin by converting O—methyl group in —OH group (Wallis AFA. 1976. Wood pulping with mono-, di- and triethanolamine. Appita 31(6): 443-448).

Those skilled in the art will know how to select acceptable quantities of compounds A and B according to the particular experimental conditions and desired output.

- 5 Typically quantities of compounds A and B are regulated such that enthalpies of reaction and enthalpies of mixture will result in an amount of energy sufficient to disrupt or break intermolecular bonds existing between cellulose, lignin and hemicelluloses, while maintaining the original or native chemical and physical molecular structures of each component.
- 10 The present invention is generally applicable to woody and plant biomass and derivatives including, but not limited to, hard and softwood including trunk, bark, branches, roots and leaves, plants and herbs, hemp, straw, vegetable waste, wood residues, woodchips, algae, papers, cardboards and other. Biomass can also be made of mixed sources of biomass.
- 15 According to a particular embodiment, the processes of the invention comprises cleaning or washing the biomass for removing any undesirable impurity, contaminants, dirt or extractable products (waxes, tannins, minerals, essential oils, pectins, vitamins and other), prior to contacting with the source of anions and/or cations. This cleaning may help to retain only the basic constituents of the biomass
- 20 (i.e. cellulose, lignin, hemicelluloses). For instance, the process may include a step intended to prepare or macerate the biomass (e.g. macerating wood chips). The washing of the biomass may be performed according to several known processes, including but not limited to, washing with or without surfactants; washing with cold water, hot water, or steam; by using ultrasounds or microwave; by using maceration
- 25 in solvents (ethanol, for example).

- The processes of the invention can be performed at room temperature (about 20°C) and ambient pressure (1 atm or about 760 mm Hg). As such, it is not necessary to add/or subtract thermal energy since such energy is produced by the added reagents and/or the biomass itself. No mechanism is required either to increase or decrease
- 30 pressure during the reaction.

The processes according to the present invention may be carried out in an open or in a closed reactor. Suitable reactors may include reactors made of stainless steel, glass, Pyrex, high density polyethylene (HDPE) or other plastics, or any suitable

material preferably resistant to corrosion, medium-high temperature and pressure. In one particular embodiment, reactions/extraction according to the invention take place in a simple unpressurized HDPE open reactor.

Consequently, the processes of the invention include the possibility to modulate
5 temperature and/or pressure besides those generated by the desired enthalpies of reaction and mixture. In particular embodiments, the process is carried inside a reactor, and the process comprises controlling the temperature, atmosphere and/or pressure inside the reactor. For instance, the temperature inside the reactor may be between about -20 °C and about 270 °C. In some embodiments, the temperature
10 inside reactor is between about 15 °C and about 150 °C. In some embodiments, the temperature inside reactor is between about 30 °C and about 140 °C. If desired, the temperature inside the reactor may be controlled and adjusted to be within desirable values using any suitable technique (e.g. cooling, heating, pressurizing, etc.). The atmosphere inside the reactor may consist of air, of a nitrogen inert atmosphere, of
15 an atmosphere free of CO₂, of an atmosphere free of O₂, etc. If desired, the atmosphere inside the reactor may be controlled and adjusted to be within desirable conditions, using any suitable technique (injection of a particular gas, elimination of undesirable gases, addition of a chemical reaction with O₂, etc.). The pressure inside the reactor may vary from about 0.003 atm (about 2 mm Hg) to about 40 atm or more
20 (e.g. 0.003, 0.005, 0.01, 0.05, 1, 2, 3, 5, 10, 20, 30, 40 ATM, etc.). In preferred embodiment, the pressure is about 1 or 2 atm. If desired, the pressure inside the reactor may be controlled and adjusted to be within desirable ranges using any suitable technique (use of a sealed reactor, creation of a vacuum or pressurization, modification of the proportions of the reactants (e.g. compound A, compound B,
25 biomass) etc.).

In some embodiments, the processes further comprise a step of decreasing viscosity of the exothermic reaction involving compound A and compound B. This can be done by adding a compound C that will decrease viscosity of the mixture and/or slow down reaction (inert or not). The compound C may be an aqueous solvent (e.g. water), a
30 non-aqueous solvent (e.g. ethanol) or a combination thereof. Typically, Compound C is added after the delignification and cellulose extraction step (Fig. 1, 180) and preferably after compound B (or after compound A, depending on the sequence both products have been added to the reaction). Compound C may be added after a certain time, allowing the reaction to occur. That period of time may be only a few
35 minutes (e.g. about 1 min, about 2 min, about 5 min, about 10 min, about 15 min,

about 30 min or more) or it may be longer (at least 15 min, at least 30 min, at least 45 min, at least 1h, at least 2h or more).

Those skilled in the art will understand that experimental conditions to be selected in the processes of the invention will vary according to numerous factors and that
5 different choices may be made by an operator. For instance, a person skilled in the art will know to avoid inappropriate choices of compounds A and B and will know to avoid poor experimental conditions that could lead to partial or incomplete realization or failure of the process or unsuccessful cellulose extraction. Examples 1-5
10 hereinafter provide examples of suitable experimental choices in response to specific objectives. A person skilled in the art will understand that at different steps of the process, experimental parameters need to be selected to reach different results. Examples of adjustable parameters that may influence final results include, but are not limited to, the followings: qualitative and quantitative choice of compound A; qualitative and quantitative choice of compound B; possibility of adding a
15 compound C, the nature and state of the biomass (wood, vegetables, variety, homogeneity, aged, rotten, etc.); whether the biomass is washed or not and the particular washing method being used; the size of the biomass (e.g. size of woodchips and sawdust); temperature and pressure conditions whether artificially increased or lowered by a user or operator; the duration of each steps; the exact
20 sequence of each step (e.g. A before B or vice versa); close vs. open reactor; pressurized or not reactor; the controlled atmosphere conditions inside the reactor (inert, CO₂ free, oxygen free), the temperature, etc.

According to particular embodiments, the processes according to the invention further comprise isolating from the cellulose pulp components contained therein. For
25 instance, it may be possible to isolate cellulose, lignin, hemicelluloses, waxes, tannins, minerals, essential oils, pectins and vitamins.

Any suitable known techniques and methods may be used for isolating these components. For instance, isolation of cellulose may comprise one or more of the following optional steps: washing step, a drying step, a bleaching step, a grinding
30 step and a sieving step. The cellulose obtained may be modified according to specific operating conditions or it can conserve all native molecular properties or it can be functionalized. Ions can be removed as for example using zinc metal to eliminate nitrate ions present in the solution. Other possible washing treatment using bicarbonate will bring cellulose at pH value ranging from 5 to 7. A second series of

washing with distilled water and potassium carbonate will remove ions and salts that would have been added through this last step.

Type I cellulose, including cellulose according to the invention, can be transformed in other allomorphes such as type II, type III and type IV cellulose by mean of simple chemical operations known to those skilled in the art (e.g. Mazza, 2009, Modification chimique de la cellulose en milieu liquide ionique et CO₂ supercritique, Université de Toulouse, France, 172 p.). Accordingly, the present invention encompasses such transformations and encompasses type II, type III and type IV celluloses deriving from cellulose I according to the invention.

10 **Figures 1, 2A and 2B** illustrate one particular embodiment for isolating cellulose according to the invention. The process (100) includes a preparation step (120). As an example, the preparation step (120) includes one or more preliminary steps before performing the process such as biomass conditioning (e.g. cleaning biomass from coarse contaminants and shredding the biomass), as well as solubilisation of compounds A and B, if need be, and the choice of experimental parameters.

The process of **Figure 1** further includes an optional biomass washing step (140). This step typically consists in eliminating undesirable contaminants, dirt and extractable products from the biomass in order to preferably retain only the basic constituents of the biomass (cellulose, lignin, hemicelluloses). The biomass washing step (140) can be done before, after or at the same time defined than the preparation step (120).

Once preparation (120) and washing (140) steps are completed, the process (100) involves a mixing step which allows the biomass to be in contact with compound A (160) as illustrated in **Figure 2A**. At this stage, the biomass (2) is put in contact with compound A (1) in a receptacle or reactor, either by adding compound A onto the biomass or by adding biomass within compound A. Bringing biomass and compound A in contact can be done using different types of reactor such as for example, continuous, counter-current or batch reactors. Addition of compound A can be done at any stage prior to delignification, such as washing and shredding stages for example.

Considering affinities of compound A (1) to penetrate biomass, the contact step (160) between biomass (2) and compound A leads to an instant combination of enthalpies of reaction and of mixture ΔH leading to exothermic reactions and swelling of the

biomass (170). At that time, one could observe raising pressures and temperatures, gaseous emission and viscosity increase of the cellulose pulp, depending on experimental parameters. At that time, there may be partial or complete modification of the biomass components.

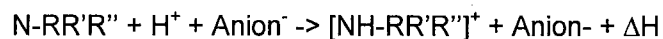
- 5 A person versed in the art will understand that the nature and the concentration of compound A, the quantity and grading of biomass, and the time or duration of the biomass and compound A contact step (160) are part of experimental parameters and may vary depending on the expected results.

- 10 A person versed in the art will also understand that putting compound A (1) in contact with biomass (2) may result in a partial or complete reaction, absorption or adsorption depending on the way contact is provoked, leaving some compound A unused or in excess within the solution.

- 15 It can then be decided to isolate or separate the soaked biomass from the compound A in solution in order to only use the soaked biomass for the next steps. It is also possible to keep the soaked biomass away for a certain time before reusing it the next steps and contacting with compound B.

- 20 Still, in the particular embodiment as illustrated in **Figures 1 and 2A**, the process (100) includes a delignification and cellulose extraction step (180) following the contact of biomass with compound A (160 and 170). According to this particular embodiment, compound B (4) is directly added on products or mixture resulting from the contact step (160) (these products being the solution that contains impregnated biomass with compound A and compound A impregnated). The addition of B can be done like the contact step (160) such as, for example, in continuous, counter-current or batch reactors. The delignification and cellulose extraction step (180) may also occur at step (160) when compound A and biomass are contacted together.

- 25 Without being bound by any theory, it is hypothesized that the delignification and cellulose extraction step (180) provokes a reaction between compound A and compound B, a reaction that may be explained by the following chemical equation when compound A is an amin or a polyamine, for example:



wherein:

N = nitrogen

R, R' and R'' = Radicals

H⁺ = Hydrogen ion

ΔH = enthalpy

- 5 This reaction between compounds A and B provoking, among other things, the possible creation of ionic liquid AB while releasing still enthalpies of mixture and of reaction ΔH.

The reaction between compounds A and B (160) allows at least partial solubilisation of hemicelluloses and lignin. At the end, the process produces a gelatinous
10 substance or cellulose pulp composed of a coloured solid substance (7) containing native or modified cellulose free from most or all lignin and a heterogeneous viscous or semi-liquid mixture (8) containing dissolved lignin and hemicelluloses. The heterogeneous viscous mixture (8) may contain several elements, such as: Compound A; Compound B; Solution AB and/or ionic liquid residues; hemicelluloses;
15 cellulose and lignin decomposition products (glucose and furfural, for example); waxes; tannins; minerals; essential oils; pectins; vitamins; other extractable products or various residues or contaminants (dirt, metallic dust or pieces, plastic dust or pieces, etc.).

In one particular embodiment as illustrated in **Figure 1** and **2B**, the process (100)
20 includes a separation/filtration step (200) to separate the solid substance (7) from the heterogeneous viscous mixture (8). In one particular implementation, the solid substance (7) and the heterogeneous viscous mixture (8) are positioned over a filter (9) allowing separation of the heterogeneous viscous mixture (8) and the solid substance (7). At the end of the filtration, the solid substance containing the cellulose
25 (12) is collected from the filter (9) while the heterogeneous viscous mixture (8) has flown through the filter.

It may be advantageous to facilitate or accelerate the separation / filtration step (200) by using a vacuum system under the filter. The filter (9) can be a sintered silica filter, a fibreglass filter, or a polyester or polymer filter. The choice of the separation /
30 filtration method is known by a person skilled in the art and is based on experimental choices. Separation (200) can be performed through filtration, press-filtration, centrifugation, evaporation or sedimentation, for example, followed by vacuum, pumping or any combination of these methods and others not listed.

- In one particular implementation, as illustrated in **Figure 1**, a washing / whitening / drying step (220) is realized following or simultaneously with the separation / filtration step (200). This step is optional and can be omitted. In order to wash the solid substance (7) at the separation / filtration step (200), the solid substance (7) can be washed in a solvent. The selected solvent is preferably neutral in regards with cellulose, lignin and hemicelluloses. As an example, water or ethanol can be considered as being neutral. If water is chosen, it may be preferable to use distilled, deionised or demineralised water in order to prevent contamination from untreated water.
- Cellulose (12) can also be whitened (220) through several methods and many different reagents such as hydrogen peroxide or hydrochloric acid, for example.
- Cellulose (12) may also be dried (220). The drying can be performed with an oven or in open air (14), for example.
- The biomass and compound A contacting step (160), the chemical separation step (180) and the separation / filtration step (200) can be performed once or several times to increase the proportion of cellulose in the solid phase (7). Accordingly, the term "**biomass**" as used herein also includes solid phases resulting from previous extractions or other steps such as the contacting step (160), the chemical separation step (180) or the separation / filtration step (200).
- It may also be useful according to the present invention to use mechanical actions (e.g. agitation, mixing, blending or the like) at certain stages of the process to increase efficiency, for example mixing the compound A and the biomass during the contacting step (160), mixing the biomass during the chemical separation step (180) or at any other step where a chemical compound, agent, reactant, or solvent is used.
- Those skilled in the art will appreciate that the present invention may provide numerous benefits or advantages compared to currently known technologies. Of course, the nature and extent of these advantages may vary depending on the choice of the particular conditions and experimental parameters (e.g. to the type and condition of the biomass being used as the starting material, the identity and amount of compound A and/or B, etc.) being used. The following provides a non-exhaustive not cumulative list of possible advantages: allows extraction of native or modified cellulose from different biomass constituents; allows extraction of native or modified lignin from different biomass constituents; allows extraction of native or modified

hemicelluloses from different biomass constituents; no external energy is necessary to feed reaction and/or modulate temperature and pressure parameters supply other than energy intrinsically contained within compounds A and B thereby permitting to implement small unit plants in areas where energy is difficult to produced, expensive,
5 rare or inexistent; the overall process is generally more compatible with medium and light industrial facilities than traditional chemical extraction processes (depending on experimental parameters); no need of water, allowing small unit plants to develop in areas where accessibility to water is difficult or inexistent; possibility to recycle portions or all of compounds A or B or C and end products, thereby allowing reducing
10 or avoiding the need for water treatment in order to respect and surpass environmental regulations; possibility to use chemical agents that are more environmentally friendly as precursors of ionic liquids; possibility to reuse or recycle part or all of end products of ionic liquids AB potentially formed; the use of low levels of enthalpies in order to reduce or avoid biomass denaturing or degradation;
15 possibility to preserve native chemical and physical properties of the cellulose, lignin and/or hemicelluloses (for example type and structure).

It is understood that the embodiment of Figures 2A and 2B is only one of many possible implementations of a suitable delignification and extraction process. A person versed in the art will understand that some steps may be optional and that the
20 step sequence may change depending on circumstances.

Isolated cellulose

The invention also concerns isolated cellulose obtained by the processes described herein. In one embodiment, the isolated cellulose comprises at least 95% w/w (dry weight) of microcrystalline cellulose (MCC) and/or less than 1% w/w (dry weight)
25 nanocrystalline cellulose (NCC) after grinding for 3 minutes after delignification, washing and drying processes.

As described hereinafter in Example 6, the cellulose of the invention comprises many distinctive, advantageous and/or useful characteristics when compared to known type I or type II cellulose. **Table 1** provides a summary.

Table 1 : Comparative characteristics of Type I cellulose according to invention and Type I Avicel PH101 (FMC Biopolymer)

Characteristics	Isolated cellulose of the Invention	Avicel PH101
FTIR Spectrum	Peak at 1730 cm^{-1}	No peak at 1730 cm^{-1}
RX spectrum	2 peaks at $2\theta=29.9$ and 38.3	No peak at $2\theta=29.9$ nor 38.3
Size and shape homogeneity	Homogenous, High percentage of fibers	Heterogeneous, low percentage of fibers
Fibers physical appearance	Regular smooth surface	Irregular surface with holes and fissures
Dispersion	Well dispersed	dispersed
Film formation 100% cellulose	Yes	No
Reactivity of alcohol functions – Degree of Substitution (DS)	DS = or < 3	N/A
Reticulation in a resin	> 90%	60%
Color	White to off-white	White
TGA	> 300°C	unknown
DMA	> 15%	unknown
Young's modulus	Increase	unknown
Swelling in water (1g in 10 ml)	200% after 20 min	53% after 20 min
Sedimentation in water (1g in 10 ml)	> 2 heures	< 5 minutes

Accordingly, another aspect of the present invention relates to an isolated cellulose of type I comprising one or more of the following characteristics:

- i) a percentage of crystalline cellulose of lower than 80% w/w;
- ii) it comprises fibers characterized by a ratio length/width ≥ 1 ;
- iii) a FTIR spectrum comprising a peak at 1730 cm^{-1} ;
- iv) a RX spectrum comprising peaks at $2\theta = 29.9$ and 38.3 ;
- v) it comprises a population of cellulose particles that is composed of at least 55% of particles having a ratio length/width greater than 3;
- vi) a rate of imperfection $\leq 110\%$;
- vii) it comprises a population of fibers having average length of about $10\text{ }\mu\text{m}$ to about $70\text{ }\mu\text{m}$;
- viii) an ability to remain evenly spread, without requiring dispersing agent, a density of 1000 fibres/mm^2 or even greater;
- ix) it comprises less than 1.5 ion per fibre;
- x) a measured conductivity of lower than $50\text{ }\mu\text{S.cm}^{-1}$;
- xi) an ability to coalesce and form a film;

- xii) an ability to improve reticulation of a resin epoxy by at least 30%;
- xiii) an ability to improve reticulation by at least 18% of a resin epoxy when compared to Avicel PH101;
- 5 xiv) a population of fibers comprising at least 50% less imperfections than a population of Avicel commercial type I cellulose fibers;
- xv) it is at least 90 % pure;
- xvi) it comprises less than 1.5% lignin;
- 10 xvii) it comprises less than 15% hemicelluloses;
- xviii) it has a pH of about 6.5;
- xix) it comprises about 5.8% w/w of moisture;
- xx) it has an onset of decomposition > 250 °C, when mixed with an epoxy resin;
- 15 xxi) it is miscible by at least 15% w/w in an epoxy resin;
- xxii) it comprises a sedimentation rate at least 20% slower than Avicel PH101;
- xxiii) it comprises swelling rate at least 125% greater than Avicel PH101;
- 20 xxiv) a degree of Substitution (DS) of alcohol functions equal to 3.

Applications

A large variety of articles of manufacture may benefit from using or incorporating the cellulose according to the invention. These uses and applications include, but are not
 25 limited to:

Cellulose: papers, fiber bedding and litter (for pets or livestock), acoustic and thermal insulation, textiles, filters, dietary fibres for human or animal nutrition.

Microcellulose :

- a) Microcrystalline cellulose: food additive (emulsifier, anticaking agent, texturizing agent, dispersing agent, stabiliser, thickener, bulking agent, glazing agent, coating agent, foaming agent, carrier, dietary fibres), excipient
 30 for pharmaceutical and cosmetic products.

- b) Amorphous microcellulose: saccharification from cellulose into glucose, ethanol production, proteins production by fermentation, emulsifying or stabilizing agent, raw material for functionalization.

Nanocellulose and/or microcellulose: Microfiltration papers for potable water, automotive, and analytical filters, oil recovery applications, biocomposites for bone replacement and tooth repair, medical barrier, sunscreens, pharmaceuticals and drug delivery, additives for foods (non-caloric food thickeners) and cosmetics (emulsion/dispersion), improved paper and building products, security papers, advanced or "intelligent" packaging (e.g. as a barrier material against oxygen, water vapour, grease/oil in food packaging), high-strength spun fibres and textiles, environmental protective clothing, additives for coatings, paints, lacquers and adhesives, reinforced polymers and innovative bioplastics, advanced reinforced composite materials, recyclable interior and structural components for the transportation industry, aerospace and transportation structures, iridescent and protective films, iridescent pigments, films for optical switching, pigments and inks, electronic paper printers, innovative coatings and new fillers for papermaking (strengthening agent), fuel cells, switchable optical filters and barriers.

Functionalized Cellulose: The hydroxyl groups (-OH) of cellulose can be partially or fully reacted with various reagents to afford derivatives with useful properties like mainly cellulose esters and cellulose ethers (-OR).

Organic Ester derivatives include:

- a) Cellulose acetate: films, plastic products (tool handles, eyeglass frames, toothbrushes), high quality textile fibres and threads, optical films for LCD technology, fibers for filter media, cigarette filters;
- b) Cellulose triacetate: Shrink and wrinkle resistant fibers, specialized photographic film, packaging, semi-permeable membrane used for water purification;
- c) Cellulose propionate: Thermoplastic, (eyeglass frames);
- d) Cellulose acetate propionate: Nail care, printing inks;
- e) Cellulose acetate butyrate: Thermoplastic (trim for automobiles, tool handles, pens, blister packaging, lacquers for outdoor surfaces, lenses, plastic films).

Inorganic Ester derivatives include:

- a) cellulose nitrate : nail polish, inks, lacquers, explosives, celluloid, propellants;
- b) Cellulose sulfate: oil recovery, paints, paper, textiles, cosmetics, microbicide.

5 Ether derivatives include:

- a) Methyl Cellulose (E461): texturing agent, emulsifying agent, thickener, stabiliser, laxative, artificial tears, wallpaper paste;
- b) Ethyl Cellulose (E462): A commercial thermoplastic used in coatings, inks, binders, and controlled-release drug tablets;
- 10 c) Ethyl methyl cellulose (E465): Emulsifying agent, thickener, stabiliser, foaming agent
- d) Hydroxyethyl cellulose: Gelling and thickening agent, drilling fluid.
- e) Hydroxypropyl cellulose (E463): thickening agent, filler, dietary fibre, anti-clumping agent, emulsifier;
- 15 f) Hydroxyethyl methyl cellulose: Production of cellulose films;
- g) Hydroxypropyl methyl cellulose (HPMC, E464): Viscosity modifier, gelling, foaming and binding agent;
- h) Ethyl hydroxyethyl cellulose (E467): Cosmetic additive (binder, emulsifying agent, stabiliser, film-forming agent, viscosity control additive);
- 20 i) Carboxymethyl cellulose (CMC, E466): Food additive (Emulsifying agent, thickener, stabiliser), personal lubricants, toothpaste, laxatives, diet pills, water-based paints, detergents, textile sizing, various paper products, lubricant in non-volatile eye drops, soil suspension polymer in laundry detergents.

25 *Additional envisioned applications:*

- Electrochemical preparation of (polyanilin) cellulose, (chlorophyll – fullerene) cellulose derivatives for bio-based photo current systems. (Mari Granström, Finland, cellulose derivatives: Synthesis, properties and application);
- Modification of cellulose surface with organo-silanes for mechanical properties of paper and its softness (Olivier Paquet – thesis);
- 30 - Use of pulps and papers and cellulose fibers processes to elaborate Li-ion batteries (Lara Jabbour – thesis);

- Elaboration of a photocatalytic paper. (Souhelia Adjimi – thesis).

Composite materials

Another aspect of the invention concerns composite materials comprising a resin and/or a hardener mixed with cellulosic material, preferably isolated cellulose as described herein. In particular embodiments, the composite material comprises many distinctive, advantageous and/or useful characteristics when compared to existing composite as shown in Example 6.

Any suitable resin and/or hardeners may be used in the composite material, according to the invention. Examples of epoxy hardeners include, but are not limited to, aliphatic polyamine, alyamino-amide, aromatic polyamine, anhydric acids, bore trifluorure complex from monoethylamin (MEA), and dicyan-diamide. Examples of epoxy resin include, but are not limited to, bisphenol-formol, phenol-novolac, cycloaliphatic, and hydantoine. Examples of polyester hardeners include, but are not limited to, methylethylketone peroxide, acetylaketon peroxide, cycloexanon and peroxide. In particular embodiments, the resin is a resin epoxy or a resin polyester. In particular embodiment, the resin is Epolam 2015 or Epon 862™.

In some embodiments, the composite material comprises a resin epoxy and more than 10% w/w, or more than 15% w/w, or more than 20 % w/w, or more than 25% w/w, or more than 30% w/w, or more than 35% w/w of cellulose. Preferably, the resin is a resin epoxy. Preferably, the cellulose is an isolated cellulose as described herein and/or obtained according to the process of the invention. In particular embodiments, the resin is a resin epoxy which comprises between about 15% to about 36% w/w of isolated cellulose according to the invention.

In some embodiments, the composite material comprises a resin epoxy and cellulose, the composing material having an improved elasticity of 15% or more, 20% or more, 30% or more, 40% or more, 50% or more, or 53% or more, when compared to a resin epoxy without said cellulose, as measured by Young's modulus.

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, numerous equivalents to the specific procedures, embodiments, claims, and examples described herein. Such equivalents are considered to be within the scope of this invention and covered by the claims appended hereto. The invention is further illustrated by the following examples, which should not be construed as further limiting.

EXAMPLES

In the following examples, these abbreviations are used:

	MXG	Mannose, Xylose, Galactose
	HMF	Hydroxymethylfurfural
5	HmO	Hemicelluloses derivatives and other products
	ASL	Acid Soluble Lignin
	AIL	Acid Insoluble Lignin
	LI1	2-Aminoethanol
	LI2	2,2'-Iminodiethanol
10	Cel	Cellulose
	Lig	Lignin

EXAMPLES 1 to 5: Cellulose extraction from woody biomass

Experimental parameters in all the following examples are described in **Table 2**
15 below.

Table 2: Experimental parameters and results

	Example 1 (Control)	Example 2	Example 3	Example 4	Example 5
Name	Reference (woodchips without use of the process)	LI1 – NO ₃	LI2 – NO ₃	LI1 – Cl	LI2 – NO ₃
Biomass	100 g of washed maple woodchips	100 g of washed maple woodchips	100 g of washed maple woodchips	100 g of washed maple woodchips	150 g of washed white birch woodchips
Grading	Between 20 and 80 mesh	Between 9 and 20 mesh	Between 9 and 20 mesh	Between 20 and 80 mesh	< 80 mesh
Compound A	none	Nitric acid (H ⁺ NO ₃ ⁻) 200 g	Nitric acid (H ⁺ NO ₃ ⁻) 200 g	Hydrochloric acid (H ⁺ Cl ⁻) 200 g	Nitric acid (H ⁺ NO ₃ ⁻) 200 ml
Incubation time with A		30 min	30 min	45 min	12 min
Compound B	none	LI1 100 g	LI2 80 g	LI1 100 g	LI2 100 ml
Incubation time with B		30 min	30 min	30 min	10 min
Final solid product	Raw woodchips (unchanged)	40 g Cel : 82,5%; Lig : 0,6%; HmO : 16,9%	40 g Cel : 84,4%; Lig : 1,3%; HmO : 14,2%	95 g Cel : 57,2%; Lig : 23,9%; HmO : 18,9%	70 g Cel : 1005%

For each example, the biomass was first chipped and washed (water and ethanol) in order to facilitate delignification and eliminate most of undesirable contaminants, dirt and extractable products.

- 5 Then, the biomass was brought together with a liquid solution of compound A, thereby allowing enthalpies of reaction and mixture to happen at least partially. After a few minutes, Compound B was added directly within the solution containing compound A and the biomass, in order to eventually form an ionic liquid AB. After a certain period of time these reactions resulted in a cellulose pulp comprising i) a solid
- 10 phase composed principally of cellulose and ii) a heterogeneous viscous mixture comprising dissolved hemicelluloses and dissolved lignin.

- Next, the viscous and solid phases were separated by filtration through a sintered silica filter. Purity was determined by the NREL protocol "LAP - Determination of Structural Carbohydrates and Lignin in Biomass" Version 2006, by Amie Sluiter *et al.*
- 15 Biomass Program. Department of Energy of the United States of America, National

Bioenergy Center, Biomass Analysis Technology Team Laboratory Analytical Procedure 143p. Portions of this procedure are substantially similar to ASTM E1758-01 "Standard Test Method for Determination of Carbohydrates in Biomass by HPLC" (ASTM E1758-01 "Standard Test Method for Determination of Carbohydrates in Biomass by High Performance Liquid Chromatography, ASTM, 2007, 5p.).

5 Samples of extractive free biomass were analysed to determine the amount of structural carbohydrates and lignin in those samples. The cellulose content was estimated from the amount of cellobiose, glucose and hydroxymethylfurfural in the samples whereas hemicelluloses were estimated from the total content in arabinose,

10 mannose-xylose-galactose, furfural and acetic acid. The amount of acid insoluble lignin (AIL) and acid soluble lignin (ASL) in the samples was also obtained following this protocol. The AIL was determined gravimetrically and the ASL by UV-visible spectroscopy.

The filtered solid phases obtained was analysed by High Performance Liquid

15 Chromatography (HPLC) to determine the breakdown in cellulose, hemicelluloses and lignin content, according to the norm of the National Renewable Energy Laboratory (NREL). The results of the analysis are displayed in **Table 3** and in **Figure 3**.

20 **Table 3:** Breakdown analysis of solid substances following biomass delignification and cellulose extraction process described in Examples 1 to 4

	Breakdown (%)		
	Cellulose	Lignin	Hemicelluloses
Example 1 (control)	49.5	22.8	27.7
Example 2	82.5	0.6	16.9
Example 3	84.4	1.3	14.2
Example 4	57.2	23.9	18.9

The results presented in **Table 3** and **Figure 3** show that the proportion of cellulose obtained with the experimental conditions described in Examples 2 to 4 is greater than in example 1 (control).

To further confirm that the samples obtained according to Examples 1 to 4 contain

25 cellulose, hemicelluloses and lignin, additional tests (HPLC, AIL, ASL) based on NREL protocol were performed using a similar procedure.

Results of the HPLC tests are presented in **Table 4** hereinafter. The results presented in Table 3 complete and validate the results presented in **Table 3**.

Table 4 : HPLC tests results based on NREL protocol

Type	Initial mass (g)	Masse (g)										Final mass (g)
		Cellobiose	Glucose	MXG	Arabinose	Acetic acid	HMF	Furfural	ASL	AIL	Ashes	
Example 1	0,2820	0,0054	0,13301	0,0579	0,0022	0,015	0,0011	0,0033	0,0032	0,0611		0,2822
Example 2	0,292493	0	0,24551	0,0097	0	0	0,0014	0	0,0026	0,0013	0,01	0,2687
Example 3	0,059652	0	0,04921	0,0065	0	0	0	0	0,0004	0		0,0561
Example 4	0,295286	0	0,16774	0,0285	0	0	0,0012	0,0012	0,0056	0,0649		0,2692

EXAMPLE 5:

- 200 g of white birch wood chips (*Betula papyrifera* var. *papyrifera*) were washed with 750 ml of tap water and heated in a microwave oven (max. setting) three times 5 minutes. After a fourth washing with 750 ml of distilled water, the chips were dried at room temperature for 3 days. The chips were then ground to pass through a 10 mesh sieve and left to macerate for an extra 5 to 6 days in two times 1000 ml of distilled ethanol. The washed biomass was again dried at room temperature for 1 more day. The chips were then finely ground and screened to pass through a 18 mesh sieve.
- 150 g of washed birch sawdust was put in a well-mixed open batch reactor made of HDPE, displaced under a fume hood. The reactor was settled semi-inclined on a platform, equipped with a bidirectional motor shaft for lateral rotation; 200 ml of concentrated nitric acid ($\approx 70\%$) was poured on the biomass. The solution was mixed during 12 minutes, allowing some time for impregnation without mixing (≈ 3 minutes in all). Mixing was done bidirectionally ($\approx 1,5$ minute clock-wise and 1,5 counter clock-wise each time). At the end of this period, 100 ml of diethanolamine (reagent grade, $\geq 98\%$) was added to the mixture. The stirring continued for another 10 minutes in the same manner but non-stop. At some point the viscosity of the mix would increase, so a thinning agent (ethanol 95%, 200 ml) was typically added 2 minutes before the end of the process. Temperature would gradually rise after the first minute of contact with nitric acid (about 120°C); temperature would then decrease to about 75°C after about 10 minutes and rise again to temperature typically below or around 100°C right after adding diethanolamine to lower again to about 60°C after about 5 minutes.
- The pulp was then washed with ethanol to isolate the solid cellulose from the heterogeneous viscous mixture. Typically at least 8 washings were performed. Cellulosic solid fraction was separated through filtration and or decantation. To reach higher level of purity, cellulose was washed with potassium carbonate and demineralised water to eliminate acidic ions, salts and sugars.
- The washed cellulose was dried at room temperature for 1 day. The cellulose typically weight between 68 g and 72 g. The cellulose was finely ground in a powder to obtain desired fraction sizes. Then, the said powder was sieved for 60 min in a Ro-Tap™ through 4 successive sieves of respectively 150 μm , 45 μm and 20 μm ,

leaving 4 different grades of cellulose powder (< 20 µm; [20, 45] µm; [45, 150] µm, > 150 µm).

EXAMPLE 6: Structural and molecular characterization of the isolated cellulose

The cellulose obtained from white birch according to the process of Example 5 was further characterized through a series of test analysis. It was also compared to commercial cellulose I and II.

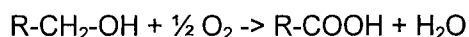
Fourier Transform Infrared spectroscopy (FTIR)

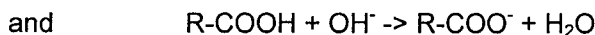
The [< 20 µm] sieved fraction of the cellulose obtained from white birch wood chips according to example 5 was subjected to a Fourier Transform Infrared Spectroscopy (FTIR) and the spectrum obtained was compared with Alpha cellulose (Sigma Aldrich) in order to validate the cellulosic nature of the cellulose of the invention. The FTIR spectrum curves of the isolated cellulose, of Alpha cellulose and an overlap of these two curves are shown in **Figure 4A**, **4B** and **4C** respectively.

Figure 4C shows a very good correlation between the curves for the Alpha cellulose and the isolated cellulose, confirming that the solid substance derived from the process of the invention is indeed cellulose. However, as shown in **Figure 4A**, the FTIR spectrum of the isolated cellulose shows at least one visible difference when compared to the FTIR spectrum of Alpha cellulose. This difference appears as a peak at 1730 cm⁻¹. As shown in **Figure 4B**, the commercial cellulose tested is a Type II cellulose does not have such a peak. The similarities and differences between the two types of celluloses are even more apparent when the two FTIR spectrum are overlapped (**Figure 4C**). The peak at 1730 cm⁻¹ represents the C=O bonds (between 1700 and 1750 cm⁻¹) of the carboxylic function. This function comes from either the C=O bond on the hemicelluloses or results from the oxidation of the isolated cellulose.

A subsequent Fehling liquor test was performed on the isolated cellulose after it has been washed thoroughly as described in Example 5. The test turned out to be negative, which means that isolated cellulose was free from sugars and thus hemicelluloses. The test confirms therefore that the 1730 cm⁻¹ peak is rather caused by an oxidation of the isolated cellulose.

The isolated cellulose has a strong propensity to oxidize, as expressed in the following equations:





Bacterial cellulose does not present such a peak although being a type I cellulose (Brown E. E., 2007, Bacterial cellulose / thermoplastic polymer nanocomposites, MSC, Washington state university, p.109) neither does the the Avicel PH101
 5 (Designing enzyme-compatible ionic liquids that can dissolve carbohydrates, Supplementary Material (ESI) for Green Chemistry, Royal Society of Chemistry 2008, 5p. Fig. 4). This strongly suggests that the peak at 1730 cm^{-1} is a unique feature of the isolated cellulose according to the invention.

Furthermore, the absence of an aromatic peak at 1505 cm^{-1} indicates that lignin has
 10 been completely removed during the cellulose extraction process (**Fig. 4A**), a measure which indirectly indicates that the isolated cellulose is free from lignin.

X-Ray diffraction

Samples of the [$< 20\text{ }\mu\text{m}$] sieved fraction of the cellulose obtained from white birch wood chips according to Example 5 were analyzed by X-ray diffraction analysis in
 15 order to determine cellulose crystalline structure and allomorphic type (I or II).

Figures 5A and 5B show typical X-ray spectrum of cellulose I (Avicel PH101, FMC Biopolymer) and cellulose II (spectrums obtained from Olga Biganska 2002, Étude physico-chimique des solutions de cellulose dans la N-methylmorpholine-N-oxyde, doctorate thesis, École des Mines, Paris).

20 The X-ray diffraction of the [$< 20\text{ }\mu\text{m}$] fraction isolated cellulose according to the invention is quite different as shown in **Figure 5C** and **Figure 5D**. Results indicate that said isolated cellulose is of type I because of the presence of 4 peaks at $2\theta = 15.1$ (1-10); 16.6 (110); 22.7 (2002); 34.5 (004) while major peaks on type II cellulose would be in $2\theta = 12.0$ (1-10); 20.0 (110); 21.9 (020) and 35 (004). This is confirmed
 25 by the correlation of spectra when overlapping type I reference and isolated cellulose (**Figure 5D**). However, 2 additional peaks are visible at $2\theta = 29.9$ and $2\theta = 38.3$. These peaks are possibly linked to reticular plans (102) for $2\theta = 29.9$ and (12-4) for $2\theta = 38.3$ (according to A. French 2013, Idealized powder diffraction patterns for cellulose polymorphs. Cellulose, August 2013) and are absent from X-Ray spectra of
 30 other type I celluloses.

Crystallinity

Several methods are used to determine crystallinity. One of them is the X-ray spectrum deconvolution. According to this method the crystallinity rate is equal to the the peak area of the lattice planes over the whole surface of the curve:

$$5 \quad \text{Percentage of Crystallinity} = (\text{Surface of peaks} / \text{Surface of the curve}) \times 100$$

Noise and artefacts have to be cleaned up in order to measure crystallinity rate of the isolated cellulose. Calculations were made using the modeling tool Mercury which allows to approximate the experimental RX curve with gaussians displaying amorphous and crystalline peaks. Crystallinity has been calculated over 4 samples and results are shown in **Table 5** below:

Table 5A: Crystallinity rates of 4 samples of isolated cellulose according to the invention

Samples	1	2	3	4	Total
Crystallinity	70,0%	71,0%	73,0%	73,9%	72,0%

Accordingly, the invention encompasses isolated cellulose characterized by percentage of crystalline cellulose equal or less than about 80 % w/w, or equal or less than about 75% w/w, or equal or less than about 74% w/w, or equal or less than about 73% w/w, or equal or less than about 72% w/w, or equal or less than about 71% w/w, or equal or less than about 70% w/w. In one particular embodiment, the crystallinity rate of said cellulose is between 70% w/w and 74% w/w.

20 Size and shape homogeneity

The fraction [20 to 45 µm] of the cellulose obtained from white birch wood chips according to Example 5 was observed under an electronic microscope at both a 200 µm and 20 µm scale with a SEM microscope and compared to Type I Avicel PHP101 cellulose (FMC, Biopolymer).

25 Microscopic imaging from scanning electron microscopy (SEM) of the isolated cellulose is shown in **Figures 6A and 6B**. **Figure 6A** displays well defined fibers, homogeneous in size and shape. In this particular picture, the mean length of the fibers is 40.4 µm (standard deviation = 30.2 µm) and the mean width is 8.1 µm (standard deviation = 4.7 µm). It was also possible to observe cellulose particles
30 having a size smaller than 1 µm (**Figure 10**).

The ratio length/width is approximately 5. Such a ratio characterizes a shape being 5 times longer than wide and thus, clearly identifies the isolated cellulose as being fibrous in contrast with other type I celluloses having high heterogeneity with few rod shaped fibres and many spherical structures (**Figures 6C and 6D**). At smaller scale (5) (**Figure 6B**), fibrils show a regular shape free from surface holes, fissures or outgrowths.

Counting on **Figure 6A** cellulose particles having a ratio Length/Width greater than 3 in a sampling zone of 400 μm x 400 μm gives the following result (**Table 5B**):

Table 5B: Fiber rate in isolated cellulose

Size of sampling zone (mm^2)	Nb particles	Particles rate per mm^2	Particles in ratio 3 : 1 or more	Percentage of fiber
0,16	155	968	85	55%

By defining a cellulose fiber as being a cellulose particle having a length at least 3 times its width, 55% of the isolated cellulose particles that were analysed can be considered as fibers.

Accordingly, the invention encompasses isolated cellulose comprising a population of (15) cellulose particles composed of at least 25%, or at least 30%, or at least 40%, or at least 45%, or at least 50%, or at least 55%, or at least 60%, of particles having a ratio length/width greater than 3. In a particular embodiment, the isolated cellulose comprises a population of cellulose particles that is composed of at least 55% of particles having a ratio length/width greater than 3.

(20) The size distribution of the length and width of the cellulose is shown in **Figures 6A and 6B** and is depicted in histograms shown in **Figures 7A and 7B**. The histograms of **Figures 7A and 7B** illustrate that 90% of all cellulose fibres lay in the length range of 10 to 70 μm which clearly is not the case for the comparison cellulose in **Figure 7C**, where most particles measure between 1 and 40 μm and are of spherical shape.

(25) Accordingly, the invention encompasses isolated cellulose comprising a population of cellulose fibers characterized by a ratio length/width ≥ 1 , or ≥ 1.5 , or ≥ 2 , or ≥ 2.5 , or ≥ 3 , or ≥ 3.5 , or ≥ 4 , or ≥ 4.5 or ≥ 5 .

Physical Appearance

Close view of electronic microscopy pictures the fraction [20 to 45 μm] of the cellulose obtained from white birch wood chips according to example 5 (**Figure 6A**), shows regularity of the cellulose fibres. Cellulose surface appears regular and smooth with little or no holes, fissures or protrusions, in contrast with other type I celluloses available on the market (**Figures 6C and 6D**) These pictures shows that said cellulose fibers have conserved their integrity when compared to existing commercial cellulose as calculated in **Table 5C**. One possible explanation is that the processes of the invention do not use strong acids to hydrolyse cellulose nor high heat and pressure as in steam explosion characterizing the Avicel PH101 cellulose which is a type I celluloses.

Table 5C: Imperfection rates of many different kinds of celluloses

Cellulose	Nb of fibers *	Number of imperfections	per fiber imperfections				
			Holes	Protuberances	Outgrowths	Fissures	Total
Avicel PH101	11,5	616	25,8	25,0	1,7	1,0	53,6
Avicel PH102	15,5	553	17,0	15,9	1,2	1,6	35,7
Avicel PH301	26,5	595	9,7	9,5	1,2	2,0	22,5
Avicel PH302	21	553	9,8	13,6	1,6	1,3	26,3
Elcema F100	17	344	7,5	11,4	0,9	0,4	20,2
Elcema F150	10,5	173	3,9	11,2	0,7	0,7	16,5
Invention	15	98	0,4	4,5	1,3	0,4	6,5

* For Avicell and Elcema, the source of cellulose is: SEM images from Ribet J., 2003. *Fonctionnalisation des excipients: application à la comprimabilité des celluloses et des saccharoses*, Thesis, Université Limoges, France, 263p, pages 128, 129, 130.

In contrast, the number of counted imperfections on the isolated cellulose in **Fig. 6B** was 23 imperfections per 50 particles which correspond to a rate of imperfection of 46%. This number is much lower to compared to the rate of imperfection for the commercial celluloses Avicel and Elcema (combined average of 134%).

Accordingly, the invention encompasses an isolated cellulose characterized by a rate of imperfection of ≤ 16 imperfection per fiber, or ≤ 15 imperfection per fiber, ≤ 12 imperfection per fiber, or or ≤ 10 imperfection per fiber, or ≤ 8 imperfection per fiber, ≤ 7 imperfection per fiber, ≤ 6 imperfection per fiber.

Accordingly, the invention encompasses an isolated cellulose characterized by ≤ 3.5 holes per fiber, ≤ 3 holes per fiber, or ≤ 2.5 holes per fiber, or ≤ 2 holes per fiber, or ≤ 1.5 holes per fiber, or ≤ 1 holes per fiber, or ≤ 0.5 holes per fiber.

Distribution / yield

Table 6 hereinafter provides the results of an average size distribution of cellulose obtained according to Example 5 (isolated cellulose) that was measured and calculated over the course of 20 cellulose purification experiments conducted on white birch wood chips.

Table 6 : Average size distribution of the isolated cellulose *

	Size of cellulose fiber (µm)			
	<20	[20 - 45]	[45 - 150]	
Biomass (% w/w dry)	6,7%	14,5%	10,7%	Total: 31,9%

* Following drying and grinding steps

Cellulose fibres greater than 150 µm in size were not computed since they were sent back to delignification. The whole processes of the invention yield about 32% w/w of dried cellulose over initial biomass, which represents up to 71% of the initial weight of the cellulose within the biomass. These results confirm the efficacy of the process when considering that cellulose represents about 45% to 50% of the whole wood biomass. Accordingly, depending of the exact experimental conditions, the present invention may envision a cellulose extraction rate between 60% and 99%, depending on experimental conditions and expected quality of the cellulose.

Accordingly, the invention encompasses process resulting in a cellulose extraction rate of at least 60%, or at least 70%, or at least 80%, or at least 85%, or at least 90% or at least 95% or at least 99% or more.

Accordingly, the invention encompasses isolated cellulose comprising fibers having average length of about 10 µm to about 70 µm. Nanoparticles should represent < 15 of the total mass.

Dispersion

Another characteristic of the cellulose obtained therein, is that this particular cellulose is not electrically charged by sodium ions as could be regular type II cellulose (due to mercerization, see also Conductivity). As a result, the isolated cellulose of the invention may be less or only slightly sensitive to electrostatic charges that may prevent it from clustering or aggregating. That isolated cellulose of type I according to the invention is therefore naturally well dispersed (**Figure 6A**) and offers properties of a non-electrostatic powder. An image computation on **Figure 6A** shows that particles

of isolated cellulose are evenly spread without aggregating, contrary to other commercial type I celluloses such as in **Figure 6C**. In particular embodiments, the isolated cellulose according to the invention exhibits an ability to remain evenly spread, without requiring dispersing agent, for instance at a density of 1000 fibres/mm² or even greater, and the present invention encompasses isolated cellulose having such characteristics.

Conductivity

Electrostatic charges can be naturally present in biomass and the corresponding ions may still be present after extraction of the cellulose. **Table 7** provides the results of analysis performed on the [$< 20 \mu\text{m}$] sieved fraction of the cellulose obtained from white birch wood chips according to example 5.

Table 7: Ions concentration

Ions	Concentration	Ion per cellobiose	Ion per fibre* (DP = 200)
K	110	0,00091	0,18
Fe	76	0,00044	0,09
Ca	760	0,00614	1,23

* A cellulose molecule with a DP of 200 (degree of polymerisation) will be charged with 1.5 ions in average.

These results show that ions are indeed present in the extracted cellulose. The results also show that the cellulose is practically uncharged (i.e. less than 1.5 ion per fibre) which proves that the processes of the current invention do not introduce any charges within the cellulose.

In addition, in one particular example, cellulose has a measured conductivity of 13 $\mu\text{S.cm}^{-1}$. This value is very close to the value of pure demineralised water confirming that, if needed, all free charges could possibly be suppressed from the cellulose.

Accordingly, the invention encompasses isolated cellulose having a conductivity lower than 100 $\mu\text{S.cm}^{-1}$, or lower than 75 $\mu\text{S.cm}^{-1}$ or lower than 50 $\mu\text{S.cm}^{-1}$, or lower than 40 $\mu\text{S.cm}^{-1}$, or lower than 25 $\mu\text{S.cm}^{-1}$, or lower than 20 $\mu\text{S.cm}^{-1}$, or lower than 15 $\mu\text{S.cm}^{-1}$. Altogether, these results confirm that it is possible to obtain isolated cellulose that hardly possesses any charges or electrolytes.

Film

According to one particular embodiment, the [$< 20 \mu\text{m}$] sieved fraction of the cellulose obtained from white birch wood chips according to Example 5, was thoroughly washing with water. The water was then left to evaporate until the
5 cellulose dries on a porous glass, without the addition of any solvents, A thin film made out of 100% pure cellulose was obtained. The bio-film was translucent, flexible but fragile and easily breakable with a thickness of about $100 \mu\text{m}$.

A similar experiment was conducted with commercial Avicel PH101 cellulose without any success what so ever. Cellulose particles would rather disseminated on the
10 surface of the glass.

Obtaining such film confirms allows the production of new biofilms being non-toxic, biocompatible, biodegradable and easy to manufacture.

Accordingly, one aspect of the present invention relates to a method for forming a film comprising: providing an aqueous mixture comprising cellulose solubilised in an
15 aqueous solvent; spreading the aqueous mixture on a surface; evaporating the solvent; and letting the cellulose coalesce and form a film.

Another related aspect of the present invention concerns a film of cellulose I. In different embodiments the film is characterized by one or more of the followings: comprising at least 100 % w/w cellulose type I; having a pH of about 6.3, a thickness
20 of about $50 \mu\text{m}$ to about $300 \mu\text{m}$.

Reactivity / functionalization

Both the [$< 20 \mu\text{m}$] and the [$20 \text{ to } 45 \mu\text{m}$] sieved fractions of the cellulose obtained from white birch wood chips according to example 5 were added to an epoxy resin (Epolam 2015™) at a proportion of 10% w/w and polymerization of the resin was
25 analyzed with a Brookfield™ viscometer.

Figure 8 depicts corresponding curves of polymerization for each of the two fractions and one commercial type I (Avicel PH101, FMC Biopolymer) when compared to the Epolam™ reference. As show in **Figure 8** and **Table 8**, there is a measurable acceleration of the reticulation time (t_{cure}) between each composite comprising
30 10 % w/w of the cellulose according to the invention when compared to a reference sample.

Table 8: Acceleration of the reticulation time (t_{cure}).

	Cellulose <20 µm	Cellulose 20-45 µm	Reference	Commercial type I (Avicel PH101)
t cure (min)	167	225	325	275
Acceleration	49%	31%	0%	15%

These results show that both fractions of the cellulose according to the invention improve significantly curing time, more so than does Avicel PH101 (FMC, Biopolymer).

- 5 Accordingly, the invention encompasses an isolated cellulose exhibiting at least 30%, or at least 35%, or at least 40%, or at least 45% or at least 49% acceleration of the reticulation of a resin epoxy when compared to reticulation of the same resin without said isolated cellulose. The invention further encompasses an isolated cellulose improving reticulation of a resin epoxy by at least 18% (e.g. 225 min vs. 275 min) or
10 bay at least 39% (e.g. 167 min vs. 275 min) when compared to Avicel PH101.

Purity

- Purity is regarded as the percentage of molecular cellulose present in the final product after thorough washing. Purity generally depends on the efficiency of the washing step. Examples 2, 3 and **Table 3** show a cellulose rate close to 85%, while
15 presence of lignin is reduced to less than 1% after 8 washing sequences with ethanol.

- Purity may also be enhanced by adding additional washing steps to eliminate acidic ions with potassium carbonate (K₂CO₃) and then sequences of washing with demineralised water to get rid of sugars and ionic salts. This treatment help obtaining
20 a highly pure cellulose (equal or close to 100%) as shown in the sections referring to film formation and FTIR analysis.

Accordingly, the invention encompasses isolated cellulose having at least 70%, or at least 75%, or at least 80%, or at least 85%, or at least 90%, or at least 95%, or at least 99%, or at least 99.9% or more purity (% w/w, as measured by MRN 300 MHz).

Color

25 During the processes of the invention, at the end of the reaction (Fig. 1, 220), the cellulose was typically off-white after washing. The cellulose obtained can be whitened by using a whitening agent, such as hydrogen peroxide, or it can be left with a certain level of impurities, depending on customer's requirements.

pH

- One gram of the [$< 20 \mu\text{m}$] sieved fraction of the cellulose obtained from white birch wood chips according to Example 5 was immersed in 10 ml of pure demineralised water. The pH of that solution was measured with a pHmeter and the value obtained was pH 6.5. This value is exactly the same than the pH measured for the demineralised water before being contacted with the cellulose (pH 6.5). This indicates that the isolated cellulose according to the invention is neutral (i.e. it does not affect the pH).

Swelling and sedimentation

- One gram of the [$< 20 \mu\text{m}$] sieved fraction of the cellulose obtained from white birch wood chips according to Example 5 and of a commercial type I cellulose (Avicel PH101, FMC Biopolymer) was immersed in 10 ml of demineralised water in a test tube and was left to sediment. After different period of time, the height of the particles remaining in suspension was measured. The results are presented in **Table 9**.

Table 9: Sedimentation and swelling

Time (min)	Height of particles remaining in suspension (mm)			Swelling (%)*		
	Invention	Avicel PH101	% difference compared to Avicel PH101	Invention	Avicel PH101	% Difference compared to Avicel PH101
0 (dry)	15	15	-	-	-	-
5	40	25	38%	166%	66%	250%
30	35	24	31%	133%	60%	222%
60	32	23	28%	113%	53%	213%
120	30	23	23%	100%	53%	188%

* Calculated as of ratio the difference between the initial height of dry cellulose (15 mm) and the measured height of the particles in suspension

- As shown, sedimentation of the isolated cellulose of the invention is slower than Avicel PH101 since more particles remained in suspension (higher height). Although not shown, it was also easier to bring back in suspension and disperse anew in the solution the cellulose of the invention compared to Avicel PH101, the later having a tendency to remain stuck at the bottom of the test tube.

Accordingly, the isolated cellulose of the invention is characterized by a sedimentation rate of at least 20% slower, or at least 25% slower, or at least 30% slower, or at least 35% slower, or at least 38% slower, than Avicel PH101.

Accordingly, the isolated cellulose of the invention is characterized by a swelling rate
5 at least 125% greater, or at least 150% greater, or at least 175% greater, or at least 200% greater, or at least 250% greater, or more than Avicel PH101.

Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) was made on the [$<45\ \mu\text{m}$] sieved fraction of the cellulose obtained from maple wood chips according to eExample 5.. Resin (Epon
10 862™) combined with a curing agent (Epikure W™) was mixed with 10% w/w of isolated cellulose. The TGA indicates the loss of mass as a function of the temperature. The TGA was carried out in high purity nitrogen and it revealed that the cellulose sample contained about 5.8 % of moisture, and that the onset of decomposition is 314 °C (**Figure 9A**). These results inform on the changes in
15 physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss).

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was made on a reference epoxy resin (Epon
20 862™) mixed with a curing agent (Epikure W™), including or not 10% the [$<45\ \mu\text{m}$] sieved fraction of the cellulose obtained from maple wood chips according to Example 5. The DMA revealed that by adding 10% w/w of cellulose to the epoxy resin, its Tg decreases from 141°C to 137°C but its storage modulus increases by 15 % (**Figure 9B**). These results are conformed to those obtained in Young's
25 modulus measurement (see below) and show the ability of the cellulose to improve mechanical properties of resins.

Young's modulus

Young's modulus, also known as the tensile modulus or elastic modulus, is a measure of the stiffness of an elastic isotropic material and is a quantity used to
30 characterize materials. It is defined as the ratio of the stress along an axis over the strain along that axis in the range of stress in which Hooke's law holds.

A Young's modulus analysis was performed on epoxy resins (Epolam 2015™) with and without the [$<45\ \mu\text{m}$] sieved fraction of the cellulose obtained from maple wood

- chips according to Example 5. Briefly, cellulose was dried for a night between 70°C and 80°C for demoiaturizing. Then, cellulose was added and mixed to Epolam 2015™ by fraction of 1% until reaching 10% or 36% of the total mass of the final product. Each addition of 1% was followed by a mechanical mixing. Once final grade
- 5 was achieved (10% or 36%), the mix resin + hardener + cellulose was inserted in a molding for 2 days, after which post curing is performed (1 hour at 70°C). Composite was then ready to be tested with a tension tester Instron™. The results of these measurements are presented in **Table 10**.

Table 10: Young's modulus analysis

Description	Max stress (Mpa)	Max deformation	Young Modulus (Mpa)	% change
Epolam 2015™ reference	74	12,6	3267	0%
Epolam 2015™ + 10% cellulose 20-45µm	55	5,8	3832	17%
Epolam 2015™ + 10% cellulose 20µm	52	5,7	3754	15%
Epolam 2015™ + 36% cellulose 20µm	27	0,87	4984	53%

10

The results of **Table 10** indicates that although the resin with cellulose is more breakable than the reference (i.e. a decrease in Max stress), Young's modulus is increased significantly (at least 15%) and by up to 50% when using 36% on the total mass of cellulose according to the invention.

- 15 Accordingly, the invention encompasses composite materials comprising a resin and/or a hardener mixed with an isolated cellulose, the composite materials having an improved elasticity when compared to composite materials without isolated cellulose. In particular embodiments, the elasticity improved by at least 15%, or at least 20%, or at least 25%, or at least 30%, or at least 40%, or at least 45%, or at
- 20 least 50%, or at least 53%, as measured by Young's modulus, when compared to a composite material without said isolated cellulose.

Reticulation of epoxy

- Composites, such as epoxy, are made of a resins combined and a fraction of hardener. Resin manufacturers always indicate the best proportion to optimize
- 25 curing. In the case of Epolam 2015™ and Epikure™ hardener, the ideal proportion is

100:32 (100 parts of resin and 32 parts of hardener). Hardener is costly and/or more toxic than resin itself and there is a demand to lower hardener proportion.

Accordingly, a the new recipe was been tested at 100:27 by using of cellulose to check how cellulose can change the ratio resin / hardener as exemplified in

5 **Table 11.**

Handling and operating resin, hardener and cellulose we made according to principles known from a person versed in the art (all experimentations and calculations were performed by the CDCQ (Centre de développement des composites du Québec), an independent organism in charge of testing new materials.

Table 11: Degree of reticulation (in %) of different epoxy mixtures at different times

	Mix	100:32	100:27	100:27	100:27	100:27	100:27
	Add-on			10% Avicel PH101	10% Invention 20 μ	10% Invention [20,45] μ	36% Invention 20 μ
Time (hr)	0	2,6	-2,3	-0,6	1,1	2	-1,1
	4	15	16	11	14	10	14
	26	72	60	52	62	61	48
	Annealing	83	52	60	91	88	63

* Annealing means postcuring

- 15 Proportion of add-on are calculated on the mass of resin was completed with 5 g of cellulose being incorporated within 50 g of resin in case of mixes with 10% addition and 17.82 g of cellulose were added in the case of mix with 36% addition.

The degree of reticulation was calculated through a FTIR analysis of peaks according to the following equation:

20
$$\text{Degree of reticulation} = 100 \times \frac{(\text{Peak}[\text{OH}]_0 / \text{Peak}[\text{=C-H}]_0 - \text{Peak}[\text{OH}]_1 / \text{Peak}[\text{=C-H}]_1)}{(\text{Peak}[\text{OH}]_0 / \text{Peak}[\text{=C-H}]_0)}$$

where:

- Peak[OH]₀ = surface of the resin FTIR peak of primary alcohol (1104 cm⁻¹)
 Peak[OH]₁ = surface of the sample FTIR peak of primary alcohol (1104 cm⁻¹)
 25 Peak[=C-H]₀ = surface of the resin FTIR reference peak (3023 / 3083 cm⁻¹)
 Peak[=C-H]₁ = surface of the sample FTIR reference peak (3023 / 3083 cm⁻¹)

The degree of reticulation refers to a measure of polymerization reaction kinetic inside the composite. Post curing is performed by heating samples for 1 hour at 70°C to accelerate chemical reactions and to be sure the polymerization has come to an end.

- 5 Both [$< 20 \mu\text{m}$] and [$20 \text{ to } 45 \mu\text{m}$] sieved fraction of the cellulose obtained from white birch wood chips according to Example 5 mixed with epoxy + hardener at 100:27 gave a better degree of reticulation than the reference at 100:32 recommended by the manufacturer (respectively 91% and 88% vs 83%). This represents a gain in both reducing hardener consumption and reticulation efficiency.
- 10 Sieved fraction [$< 20 \mu\text{m}$] sieved fraction of the cellulose obtained from white birch wood chips according to Example 5 at up to 36% w/w also improved the degree of reticulation of a reference at 100:27 (68% vs 52%). The reticulation at the greatest tested ratio (100:32) was still acceptable and not too remote from the manufacturer's recommendation (68% vs 88%).
- 15 By contrast, a commercial type I cellulose (Avicel PH101, FMC Biopolymer) mixed with epoxy+hardener at 100:27 reduced the degree of reticulation of the reference at 100:32 (60% vs 88%), but slightly improved it at 100:27 (60% vs 52%).

Degree of Substitution (DS)

- 20 Cellulose is a polymer made of cellobiose units. Each cellobiose is made of 2 glucoses and each glucose possesses 3 alcohols: 1 primary alcohol and 2 secondary alcohols. Oxidation of these 3 alcohols indicates the Degree of Substitution of these alcohols.

- 25 In various experiments, the isolated cellulose of the invention was oxidized with $\text{NiO}(\text{OH})$ (obtained through oxidation of Ni^{2+} by ClO^-) in order to change the alcohols within the isolated cellulose to acidic functions for increasing the degree of substitution. Next the oxidized cellulose was subjected to a Fourier Transform Infrared Spectroscopy (FTIR) the spectrum obtained was compared to the spectrum of non-oxidized cellulose. The spectra are shown in **Figures 11A, 11B and 11C**.
- 30 **Figure 11C** displays the overlap of both FTIR spectrum where Sample 1 refers to oxidized cellulose while sample 2 refers to initial cellulose non oxidized showing changes in the peaks. **Table 12** summarizes the main changes.

Table 12: DS determination through FTIR comparison

Peak	location (cm ⁻¹)	Assignment	Cellulose	
			Initial	Oxidized
1	2920	CH ₂	Yes	No
2	1730	C=O	Weak	Strong
3	1107	primary OH	Yes	No
4	1056	primary OH	Yes	No

As observed in **Table 12**, peaks related to alcohol functions (peaks number 3 and 4) have disappeared in the oxidized cellulose. Furthermore, peak 1 related to the CH₂ bonds have also disappeared. On the contrary, peak number 2 (C=O of acidic function) becomes predominant indicating that all alcohol functions (n=3) have been changed to acidic functions and thus, the degree of substitution DS is equal to 3.

Accordingly, the invention encompasses isolated cellulose comprising a degree of Substitution (DS) of alcohol functions equal to 3.

10

* * *

Headings are included herein for reference and to aid in locating certain sections. These headings are not intended to limit the scope of the concepts described therein under, and these concepts may have applicability in other sections throughout the entire specification. Thus, the present invention is not intended to be limited to the embodiments shown herein but is to be accorded the widest scope consistent with the principles and novel features disclosed herein.

15

Unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, concentrations, properties, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about". At the very least, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the present specification and attached claims are approximations that may vary depending upon the properties sought to be obtained. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the embodiments are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain

20

25

certain errors resulting from variations in experiments, testing measurements, statistical analyses and such.

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof
5 will be suggested to persons skilled in the art.

CLAIMS:

1. A process for the production of a cellulose pulp, comprising:
 - providing a biomass comprising cellulose, hemicelluloses and lignin;
 - contacting the biomass with a source of anions and a source of cations,
5 wherein said source of anions and said source of cations are selected to react exothermically with the biomass and with each other;
 - allowing exothermic reactions under conditions and for a period of time sufficient to break intermolecular bonds existing between lignin, cellulose and hemicelluloses;
 - 10 – obtaining a cellulose pulp comprising solubilised hemicelluloses and solubilised lignin.
2. The process of claim 1, wherein said biomass provides at least a portion of said source of anions.
3. The process of claim 1 or 2, wherein said cellulose pulp comprises: i) a solid
15 phase composed principally of cellulose and ii) a heterogeneous viscous mixture comprising said solubilised hemicelluloses and said solubilised lignin.
4. A process for the production of a cellulose pulp, comprising:
 - providing a biomass comprising cellulose, hemicelluloses and lignin;
 - providing a source of anions A and a source of cations B, wherein said
20 source of anions A and said source of cations B are anionic precursors of an ionic liquid of formula AB, and wherein said source of anions A and source of cations B are selected to react exothermically with the biomass and with each other;
 - contacting the biomass with the source of anions A and with the source
25 of cations B, wherein said contacting is carried out under conditions and for a period of time allowing the formation of said ionic liquid AB, and wherein said contacting is exothermic and breaks intermolecular bonds existing between lignin, cellulose and hemicelluloses;
 - obtaining a cellulose pulp comprising i) a solid phase composed
30 principally of cellulose and ii) a heterogeneous viscous mixture comprising solubilised hemicelluloses and solubilised lignin.
5. The process of any one of claims 1 to 4, further comprising isolating from said cellulose pulp a component selected from the group consisting of: cellulose, lignin, hemicelluloses, waxes, tannins, minerals, essential oils, pectins, and vitamins.

6. The process of any one of claims 1 to 5, wherein the biomass is contacted and allowed to react with the source of anions prior to being contacted with the source of cations.
7. The process of any one of claims 1 to 5, wherein the biomass is contacted
5 and allowed to react with the source of cations prior to being contacted with the source of anion.
8. A process for isolating cellulose from biomass, comprising :
- a) providing a biomass comprising cellulose, hemicelluloses and lignin;
 - b) contacting the biomass with a compound A for impregnating at least
10 partially said biomass and for obtaining an impregnated acidic biomass, wherein compound A is a source of anions and wherein compound A reacts exothermically with the biomass;
 - c) contacting the impregnated acidic biomass with a compound B,
15 wherein compound B is a source of cations and wherein compound B reacts exothermically with compound A impregnated within the acidic biomass;
 - d) allowing exothermic reactions under conditions and for a period of time
20 sufficient to break intermolecular bonds existing between lignin, cellulose and hemicelluloses and produce a cellulose pulp comprising solubilised hemicelluloses and solubilised lignin;
 - e) isolating cellulose from said pulp.
9. The process of claim 8, further comprising an intermediary step of decreasing viscosity of the exothermic reaction of step d) prior to step e).
10. The process of claim 9, wherein decreasing viscosity comprises adding an
25 aqueous and/or a non-aqueous solvent.
11. The process of claim 10, wherein the aqueous or non-aqueous solvent is selected from the group consisting of water and ethanol.
12. The process of any one of claims 8 to 11, further comprising a step of
30 separating the impregnated acidic biomass from non-impregnated compound A prior to contacting the impregnated acidic biomass with compound B.
13. The process of claim 12, wherein said separating comprises a filtration.

14. The process of any one of claims 8 to 13, wherein step e) of isolating cellulose comprises one or more of a washing step, a drying step, a bleaching step, a grinding step, a sieving step and a milling step.
15. The process of any one of claims 8 to 14, wherein said contacting step a) and/or contacting step b) comprises pouring, pulverizing, spraying, atomizing, injecting, steaming, mixing and/or sprinkling compound A and/or compound B.
16. The process of any one of claims 8 to 15, wherein cellulose to be isolated at step e) is cellulose of Type I.
17. The process of any one of claims 1 to 16, wherein said process is carried inside a reactor, and wherein the process comprises controlling the temperature, atmosphere and/or pressure inside the reactor.
18. The process of claim 17, wherein the controlled temperature inside the reactor is between about 15 °C and about 150 °C.
19. The process of claim 17 or 18, wherein the controlled atmosphere inside the reactor is selected from the group consisting of air, a nitrogen inert atmosphere, an atmosphere free of CO₂ and an atmosphere free of O₂.
20. The process of any one of claims 17 to 19, wherein the controlled pressure inside the reactor is about 1 atm.
21. The process of any one of claims 1 to 20, wherein the source of anions is selected from the group consisting of hydrochloric acid, acetic acid, formic acid, phosphoric acid, p-toluen sulfonic acid and nitric acid.
22. The process of any one of claims 1 to 21, wherein the source of anions is a liquid.
23. The process of any one of claims 1 to 22, wherein the source of cations is selected from the group consisting of amines, polyamines, phosphines and polyphosphines.
24. The process of any one of claims 1 to 22, wherein the source of cations is a chemical compound selected from the group consisting of 2-Aminoethanol, 2,2'-Iminodiethanol and 2,2',2-nitrilotriethanol.

25. The process of any one of claims 1 to 22, wherein the source of cation is 2-Aminoethanol or 2,2'-Iminodiethanol.
26. The process of any one of claims 1 to 25, wherein the source of cations is a liquid.
- 5 27. The process of any one of claims 1 to 26, wherein the source of anions and the source of cations are a single zwitterionic compound.
28. The process of claim 27, wherein said zwitterion is selected from the group consisting of amino acids, arsenobetaine, betaine, bicine, ceftazidime, cephaloridine, edelfosine, ilsoionic point, miltefosine, perifosine, quinonoid zwitterion, tricine, and
10 trimethylglycine.
29. The process of any one of claims 1 to 28, wherein the biomass is a woody or a plant biomass.
30. The process of any one of claims 1 to 28, wherein the biomass is selected form the group consisting of: hardwood, softwood, wood residues, woodchips, trunk,
15 bark, branches, roots, leaves, whole plants, hemp, corn stalk, peat, straw, vegetable waste, algae, papers, and cardboards.
31. The process of any one of claims 1 to 30, further comprising cleaning or washing the biomass provided for removing any undesirable impurity prior to said contacting.
- 20 32. An isolated cellulose obtained according to the process of any one of claims 8 to 31.
33. An isolated cellulose characterized by a FTIR spectrum that is distinguishable from the FTIR spectrum for cellulose type II.
34. The isolated cellulose of claim 33, wherein the FTIR spectrum of said
25 isolated cellulose is distinguishable when overlapped with the FTIR spectrum for cellulose alpha as illustrated in Figure 4C.
35. The isolated cellulose of claim 33, wherein said isolated cellulose is of type I and wherein it is characterized by the FTIR spectrum of Figure 4A.
36. The isolated cellulose of any one claims 33 to 35, wherein the FTIR spectrum
30 of said isolated cellulose is characterized by a peak at 1730 cm^{-1} .

37. An isolated cellulose characterized by a X-ray spectrum distinguishable from the X-ray spectrum for cellulose type II.
38. The isolated cellulose of claim 37, wherein the X-ray spectrum of said isolated cellulose is distinguishable when overlapped with the X-ray spectrum for cellulose of type I as illustrated in Figure 5D,
39. The isolated cellulose of claim 37 or 38, wherein the X-ray spectrum of said isolated cellulose comprises a peak at $2\theta = 15,0$ (1-10), a peak at $2\theta = 16,6$ (110), a peak at $2\theta = 22,7$ (200) and a peak at $2\theta = 34,5$ (004).
40. The isolated cellulose of any one of claims 37 to 39, wherein the X-ray , with two peaks at $2\theta = 29,9$ and $2\theta = 38,3$.
41. An isolated cellulose, wherein said cellulose comprises a population of particles composed of at least 30 % of particles having a ratio length/width greater than 3.
42. The isolated cellulose of claim 41, wherein said population of cellulose particles is composed of at least 55% of particles having a ratio length/width greater than 3.
43. An isolated cellulose, characterized by a rate of imperfection of $\leq 110\%$, wherein a rate of imperfection is defined as a total number of holes, protuberances, outgrowths and fissures identified in a population of cellulose particles, that number being divided by the total number of particles in said population then multiplied by 100.
44. An isolated cellulose, wherein said cellulose is of type I and wherein it comprise one or more of the following characteristics:
- i) a percentage of crystalline cellulose of lower than 80% w/w;
 - ii) it comprises fibers characterized by a ratio length/width ≥ 1 ;
 - iii) a FTIR spectrum comprising a peak at 1730 cm^{-1} ;
 - iv) a RX spectrum comprising peaks at $2\theta = 29,9$ and $38,3$;
 - v) it comprises a population of cellulose particles that is composed of at least 55% of particles having a ratio length/width greater than 3;
 - vi) a rate of imperfection $\leq 110\%$;

- vii) it comprises a population of fibers having average length of about 10 μm to about 70 μm ;
- viii) an ability to remain evenly spread, without requiring dispersing agent, a density of 1000 fibres/ mm^2 or even greater;
- 5 ix) it comprises less than 1.5 ion per fibre;
- x) a measured conductivity of lower than 50 $\mu\text{S}.\text{cm}^{-1}$;
- xi) an ability to coalesce and form a film;
- xii) an ability to improve reticulation of a resin epoxy by at least 30%;
- 10 xiii) an ability to improve reticulation by at least 18% of a resin epoxy when compared to Avicel PH101;
- xiv) a population of fibers comprising at least 50% less imperfections than a population of Avicel commercial type I cellulose fibers;
- 15 xv) it is at least 90 % pure;
- xvi) it comprises less than 1.5% lignin;
- xvii) it comprises less than 15% hemicelluloses;
- xviii) it has a pH of about 6.5;
- xix) it comprises about 5.8% w/w of moisture;
- 20 xx) it has an onset of decomposition > 250 $^{\circ}\text{C}$, when mixed with an epoxy resin;
- xxi) it is miscible by at least 15% w/w in an epoxy resin;
- xxii) it comprises a sedimentation rate at least 20% slower than Avicel PH101;
- 25 xxiii) it comprises swelling rate at least 125% greater than Avicel PH101;
- xxiv) a degree of Substitution (DS) of alcohol functions equal to 3.

45. The isolated cellulose of any one of claims 32 to 44, wherein said isolated cellulose is extracted from woody or a plant biomass.

- 30 46. A composite material comprising a resin and/or a hardener mixed with an isolated cellulose according to any one of claims 32 to 45.

47. The composite material of claim 46, said composite material comprising a resin epoxy and more than 15 % w/w of said cellulose.

48. The composite material of claim 46 or 47, comprising an improved elasticity of at least 15% as measured by Young's modulus when compared to a composite material without said isolated cellulose.

49. A composite material comprising a resin and/or a hardener and at least 15 %
5 w/w of cellulose.

1 / 19

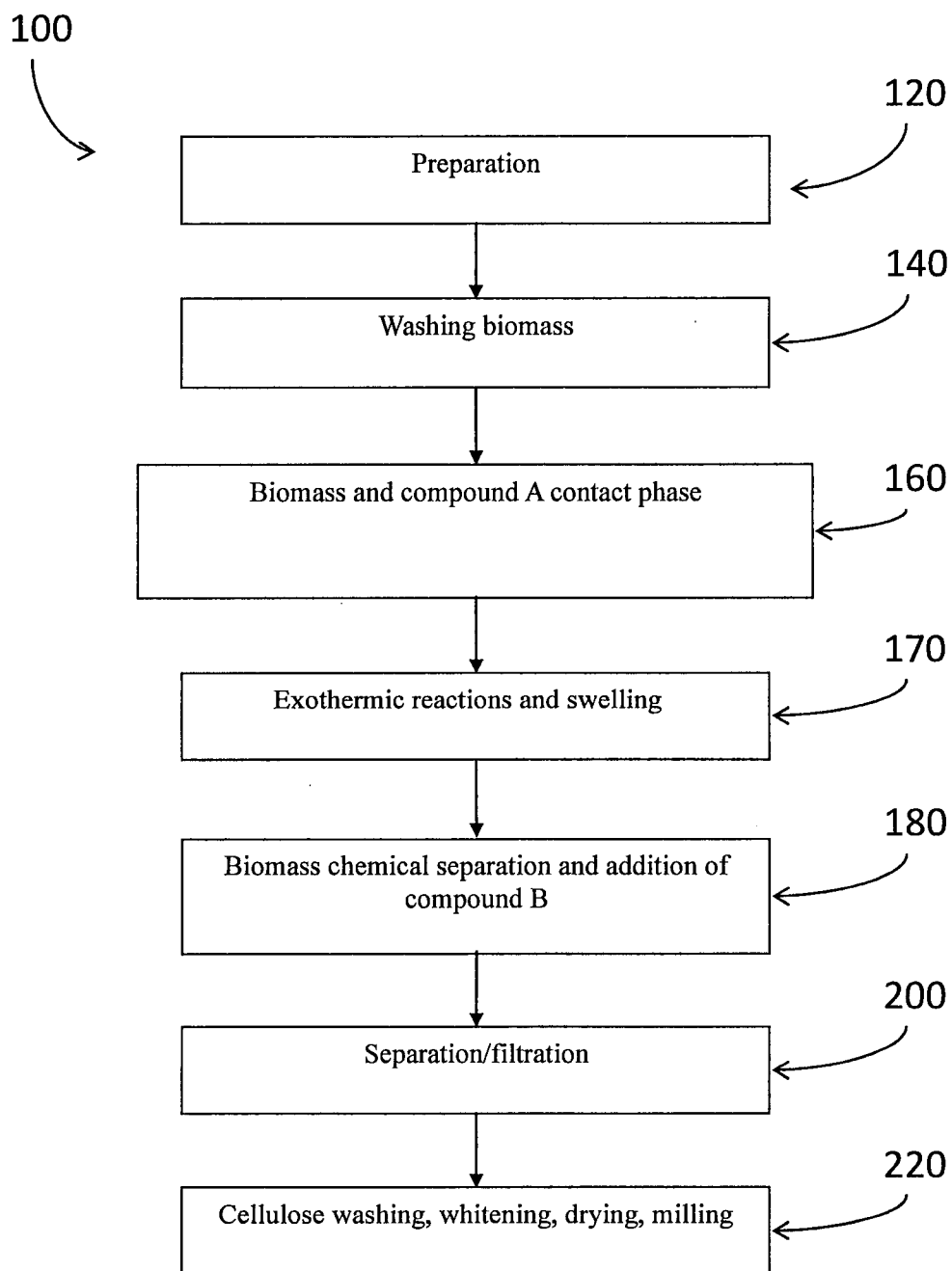


FIGURE 1

2 / 19

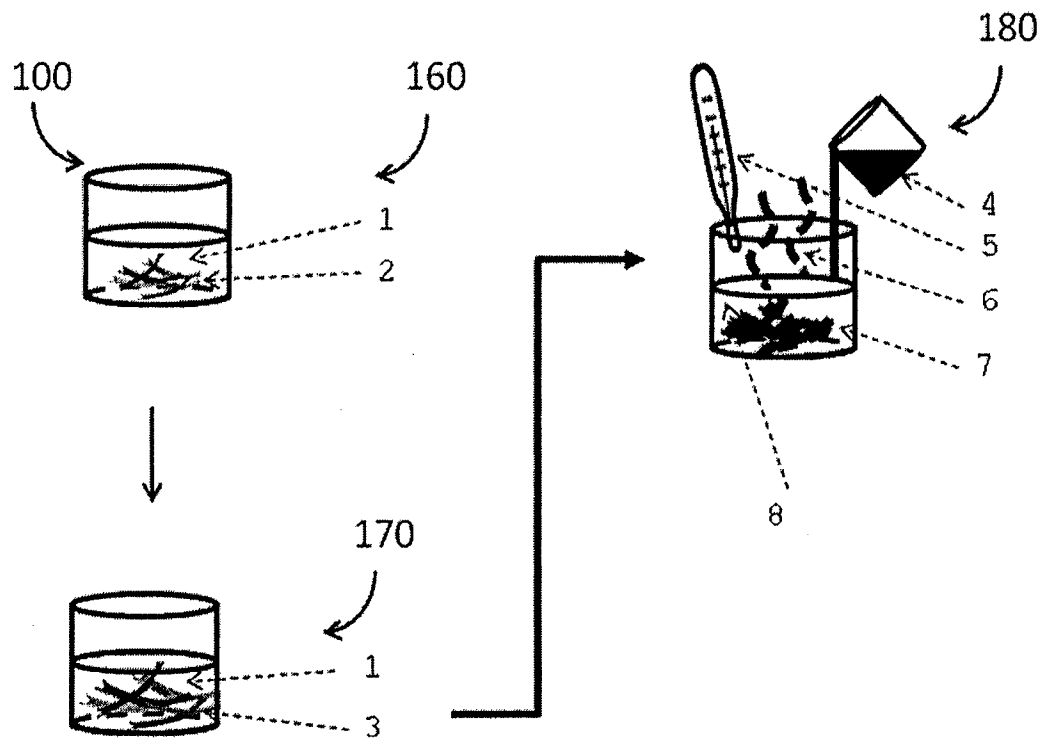


FIGURE 2A

3 / 19

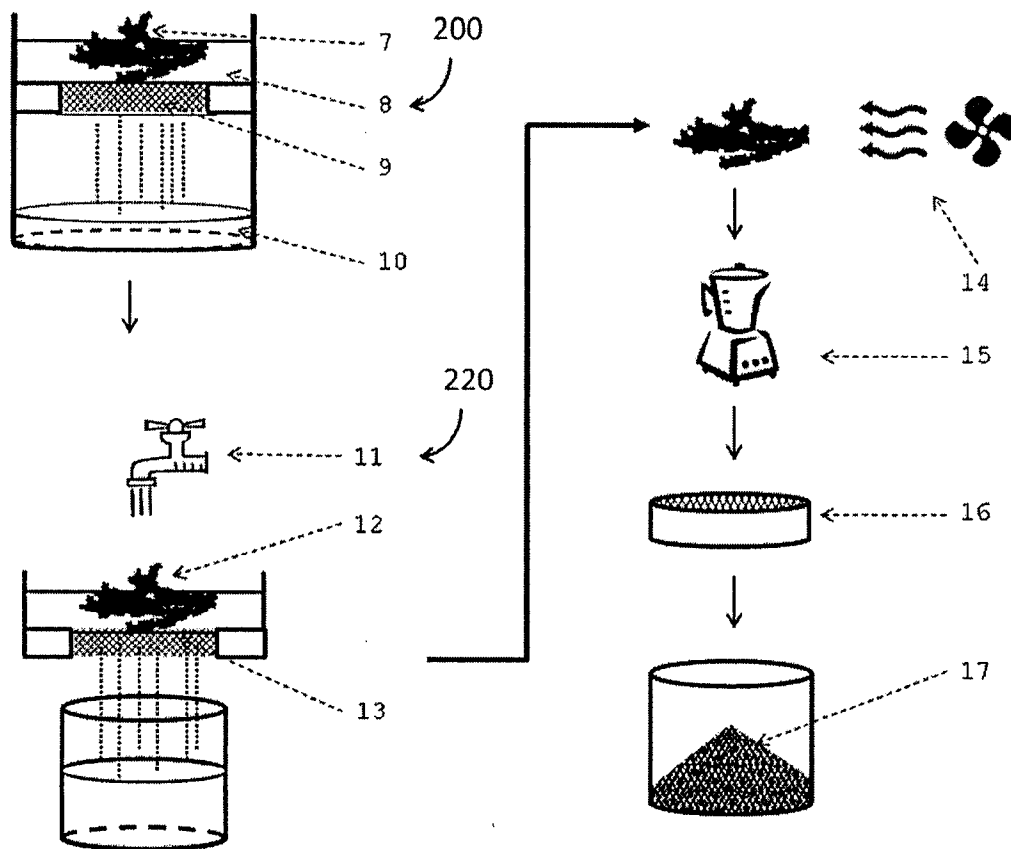


FIGURE 2B

4 / 19

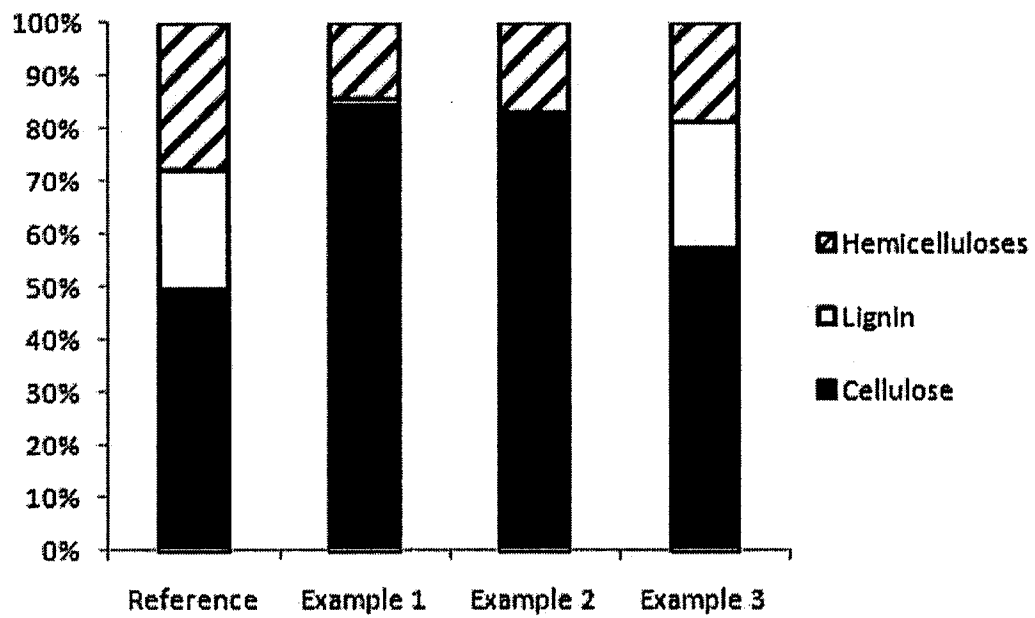


FIGURE 3

5 / 19

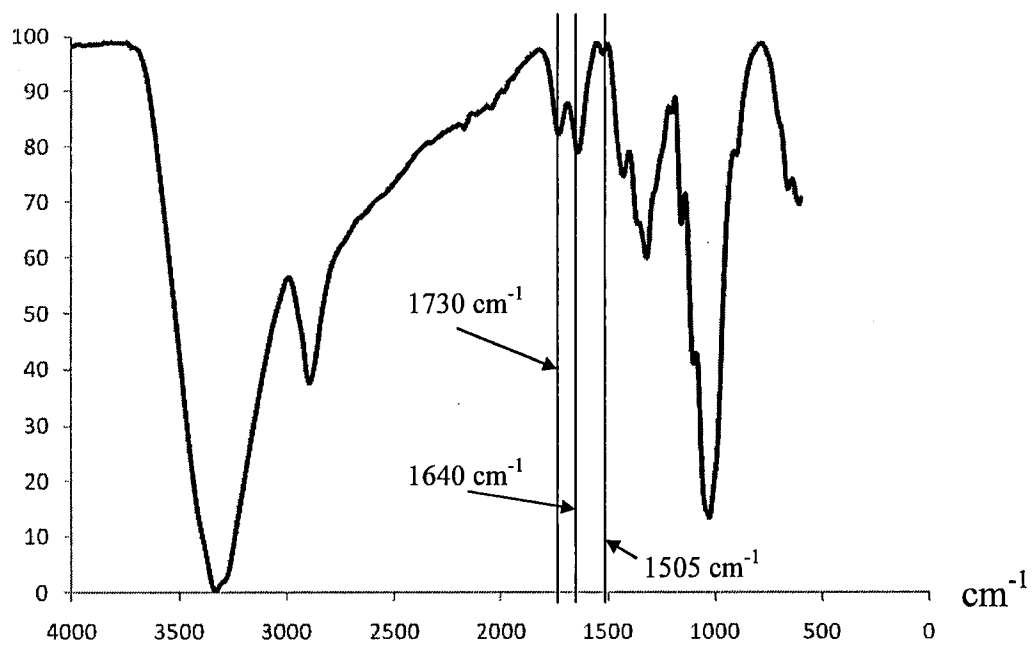


FIGURE 4A

6 / 19

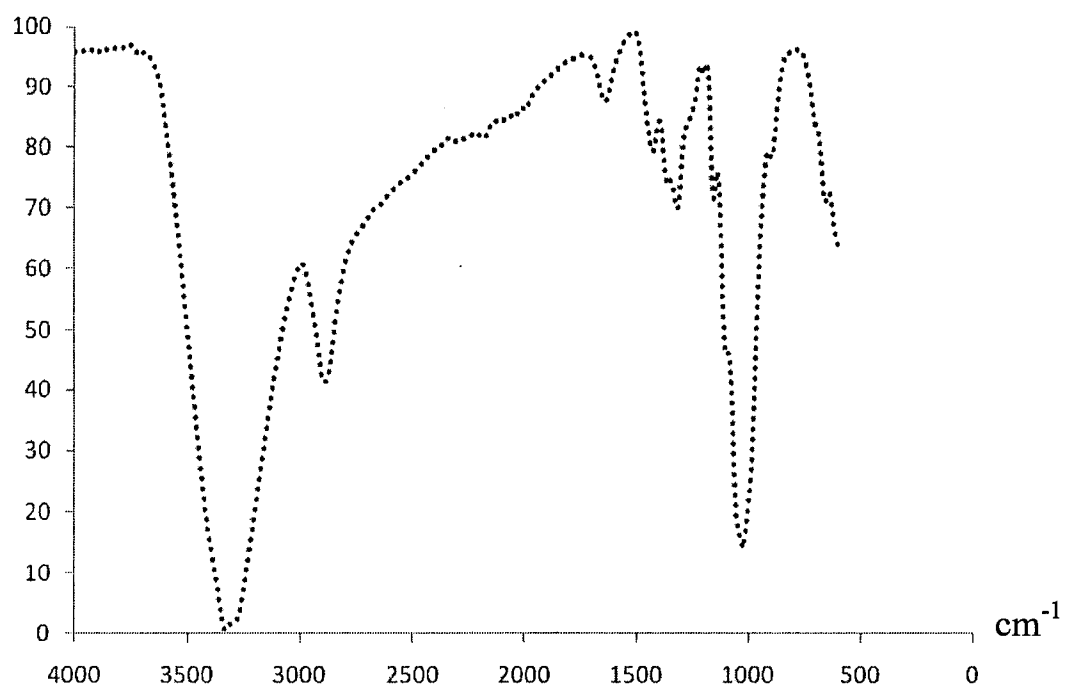


FIGURE 4B

7 / 19

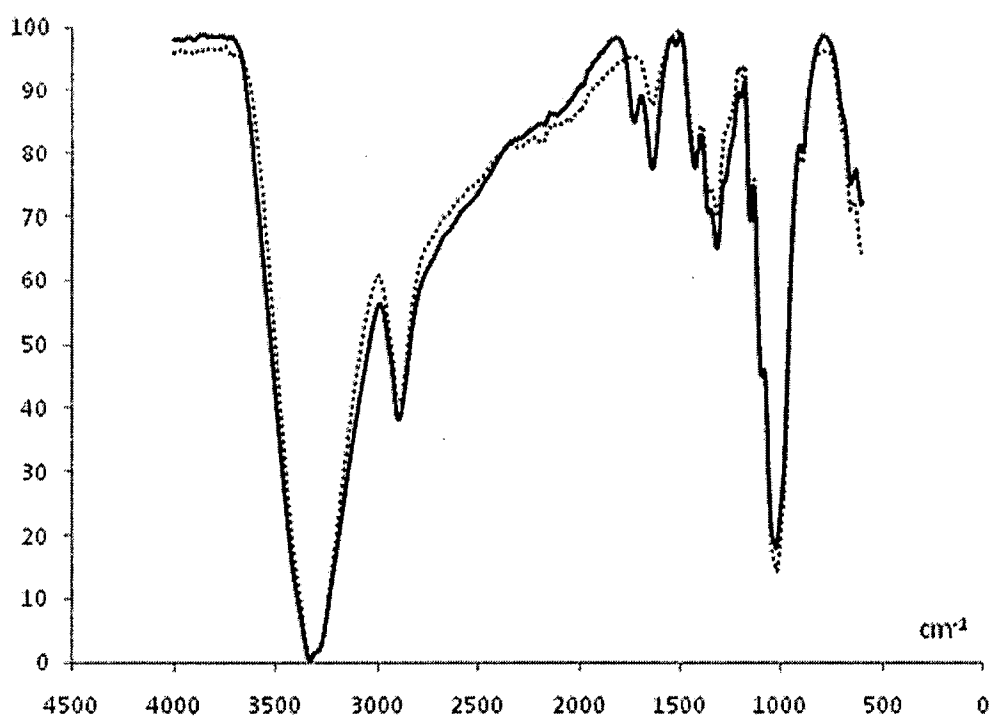


FIGURE 4C

8 / 19

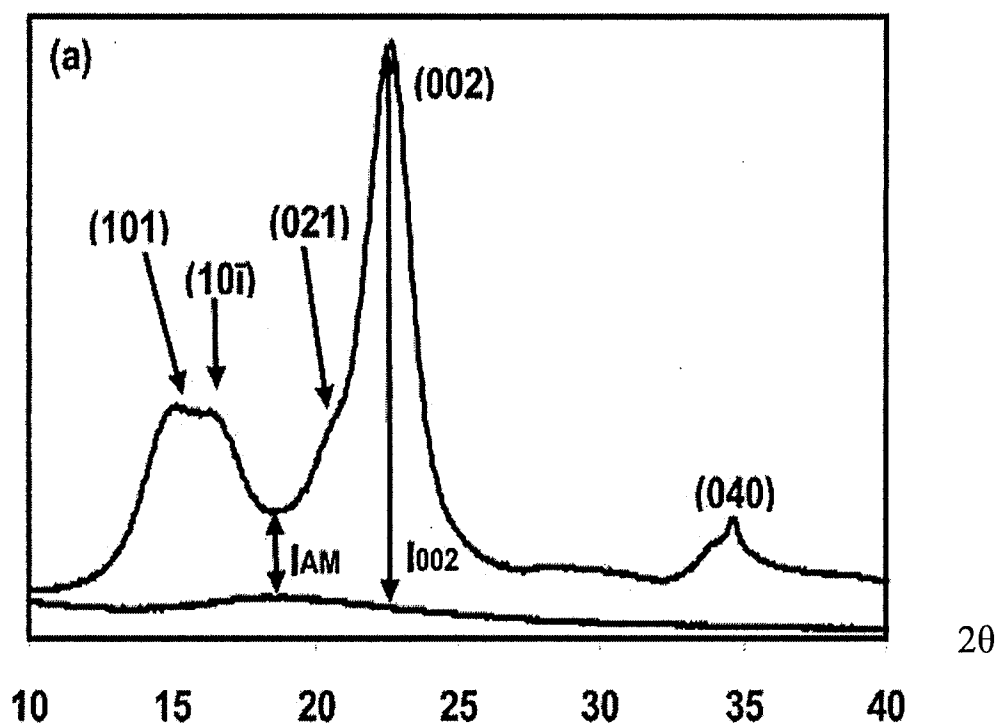


FIGURE 5A

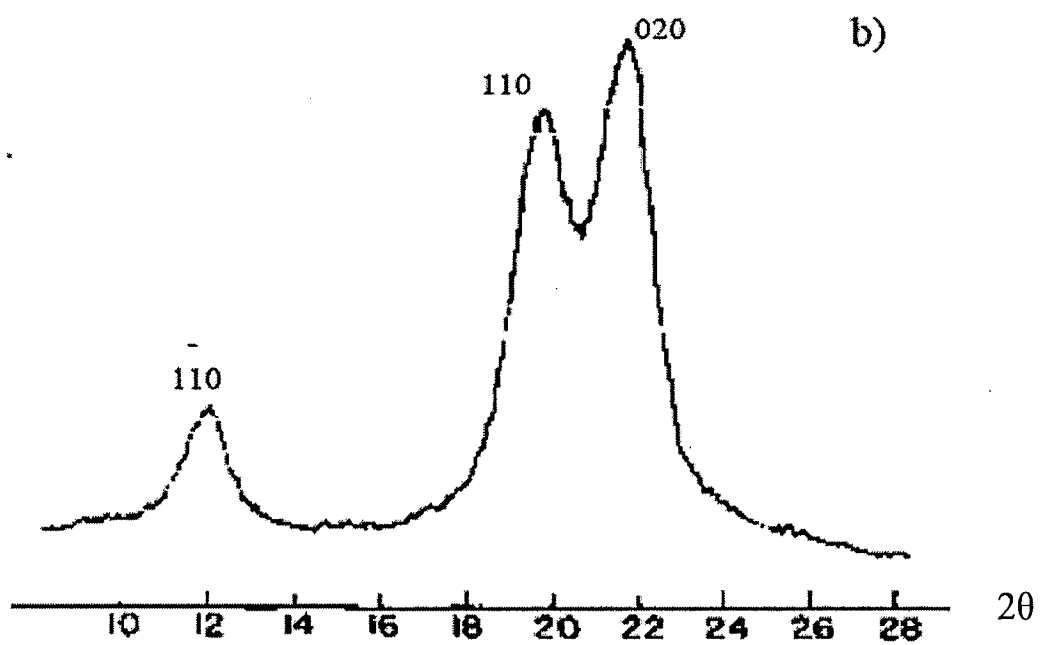


FIGURE 5B

9 / 19

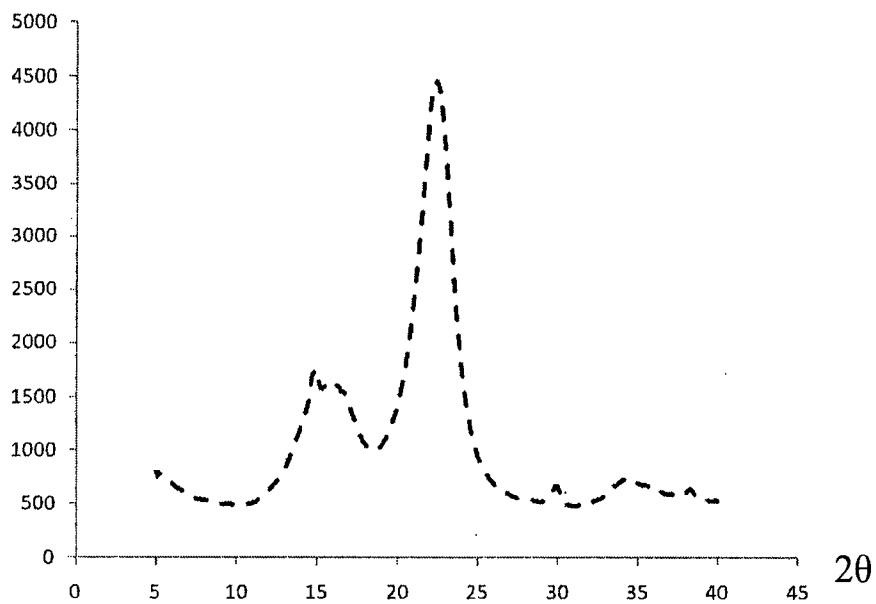


FIGURE 5C

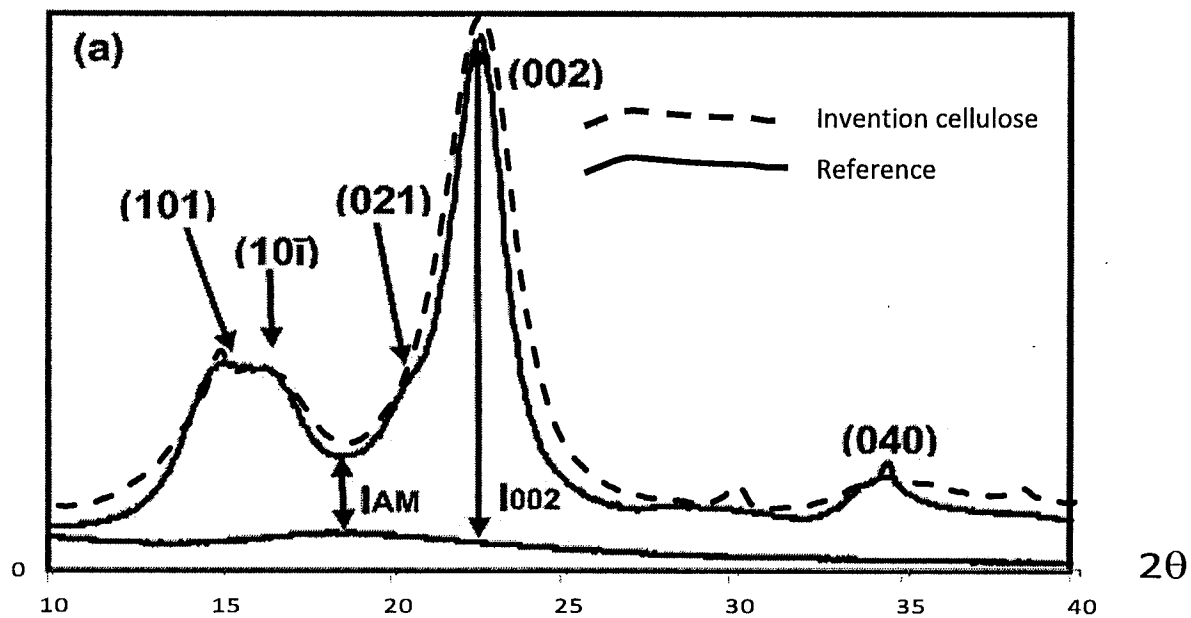


FIGURE 5D

10 / 19

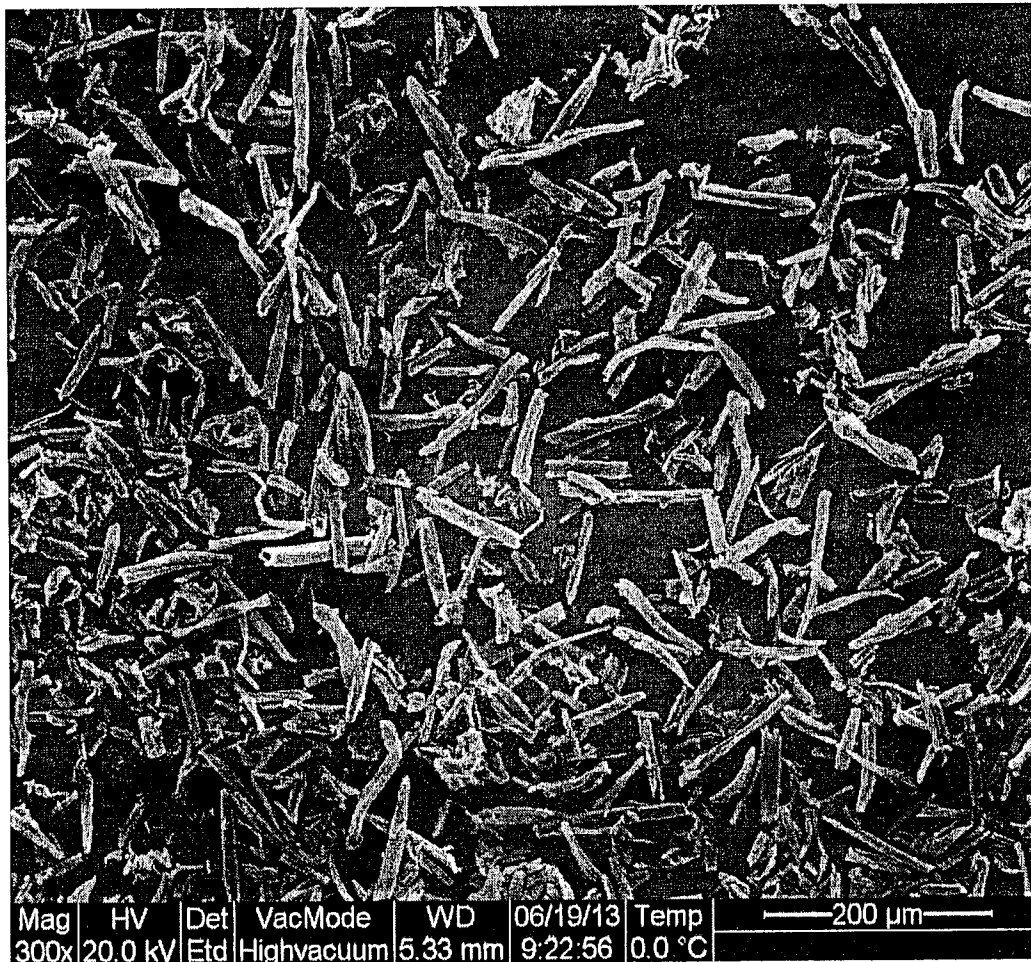


FIGURE 6A

11 / 19

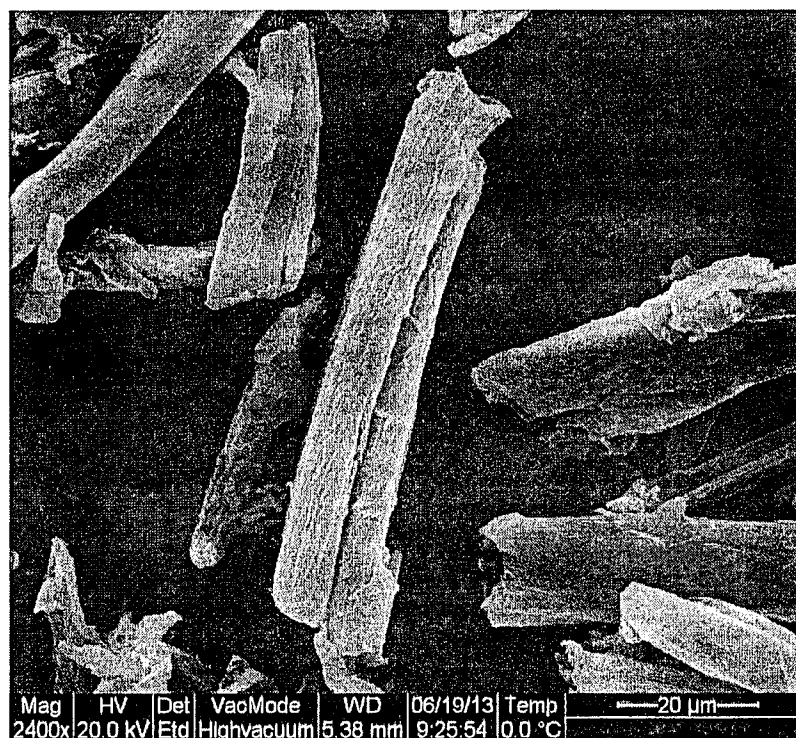


FIGURE 6B

12 / 19

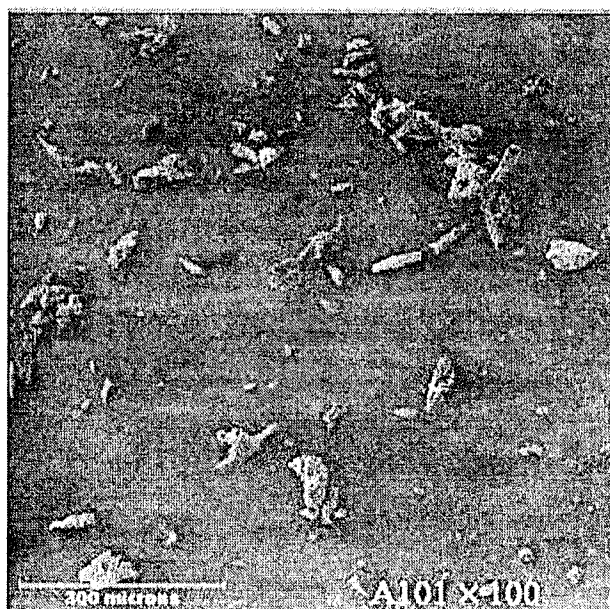


FIGURE 6C



FIGURE 6D

13 / 19

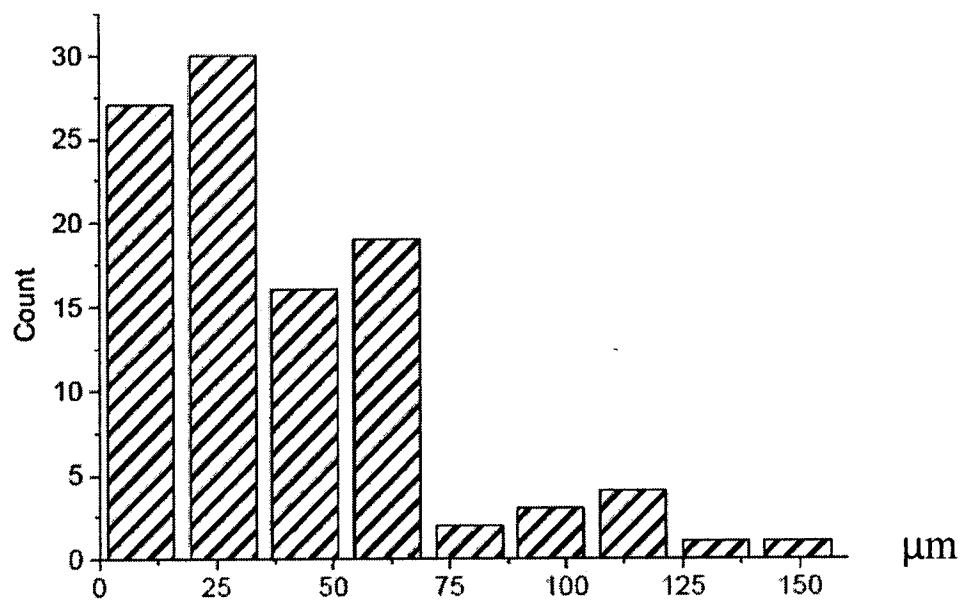


FIGURE 7A

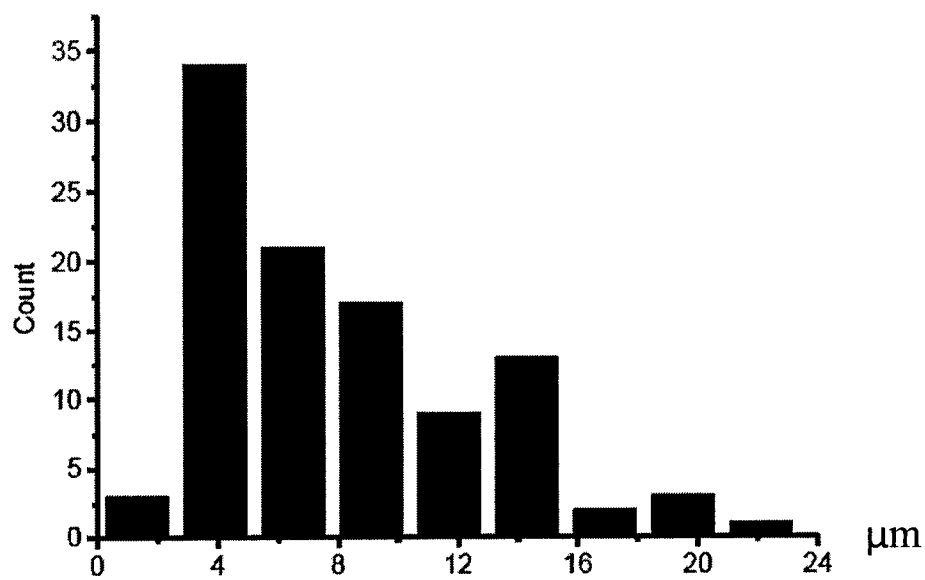


FIGURE 7B

14 / 19

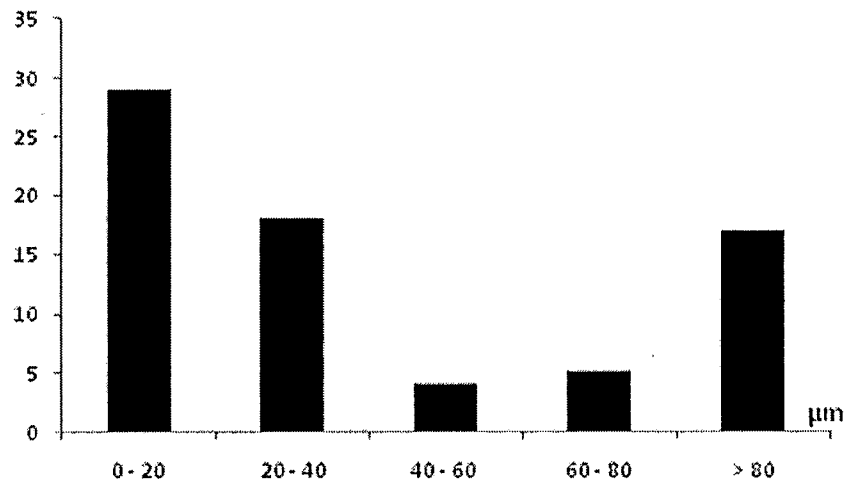


FIGURE 7C

15 / 19

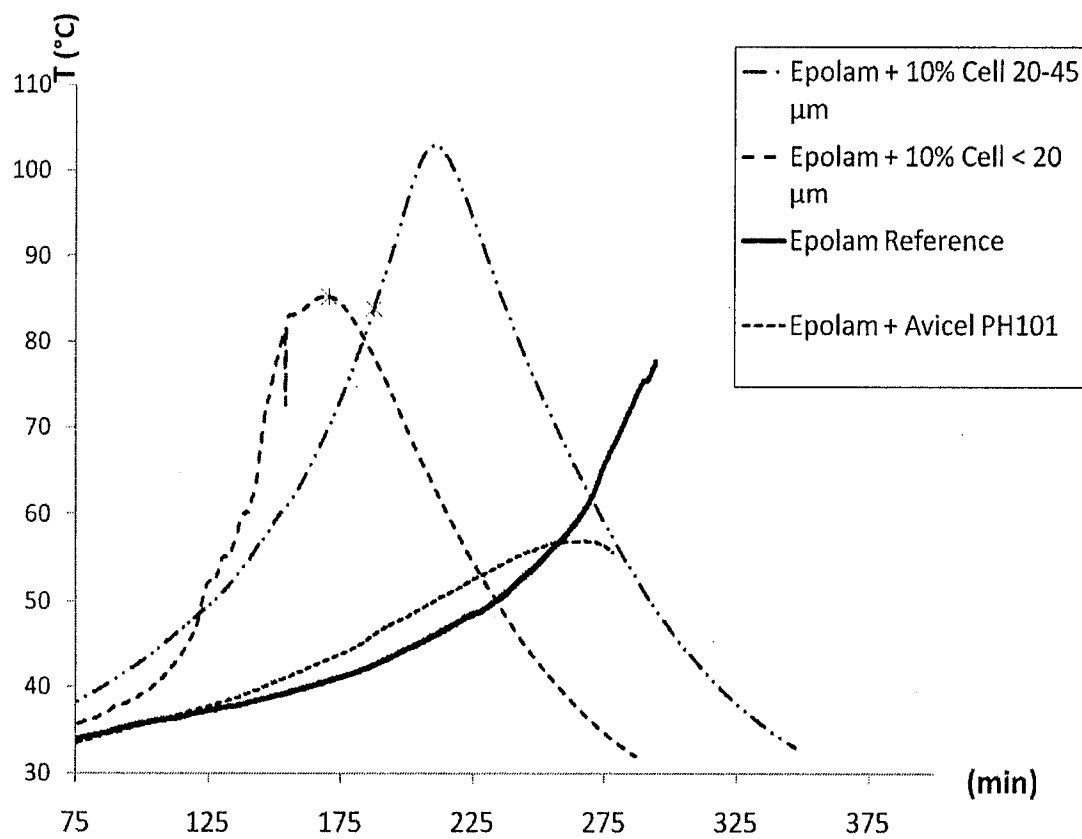


FIGURE 8

16 / 19

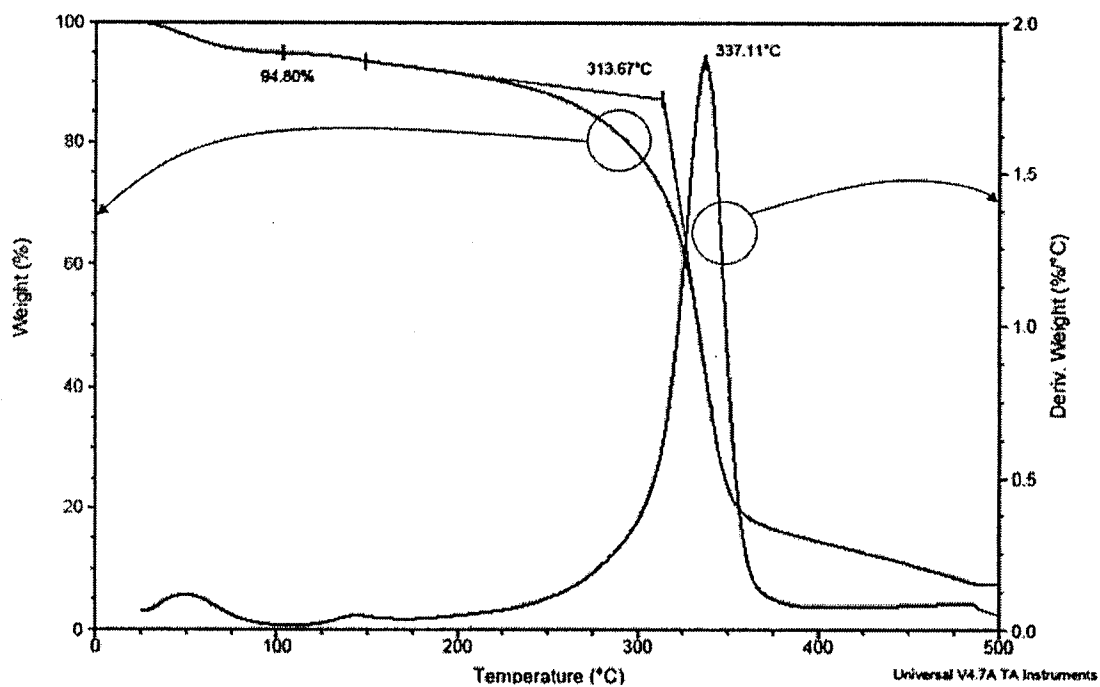


FIGURE 9A

17 / 19

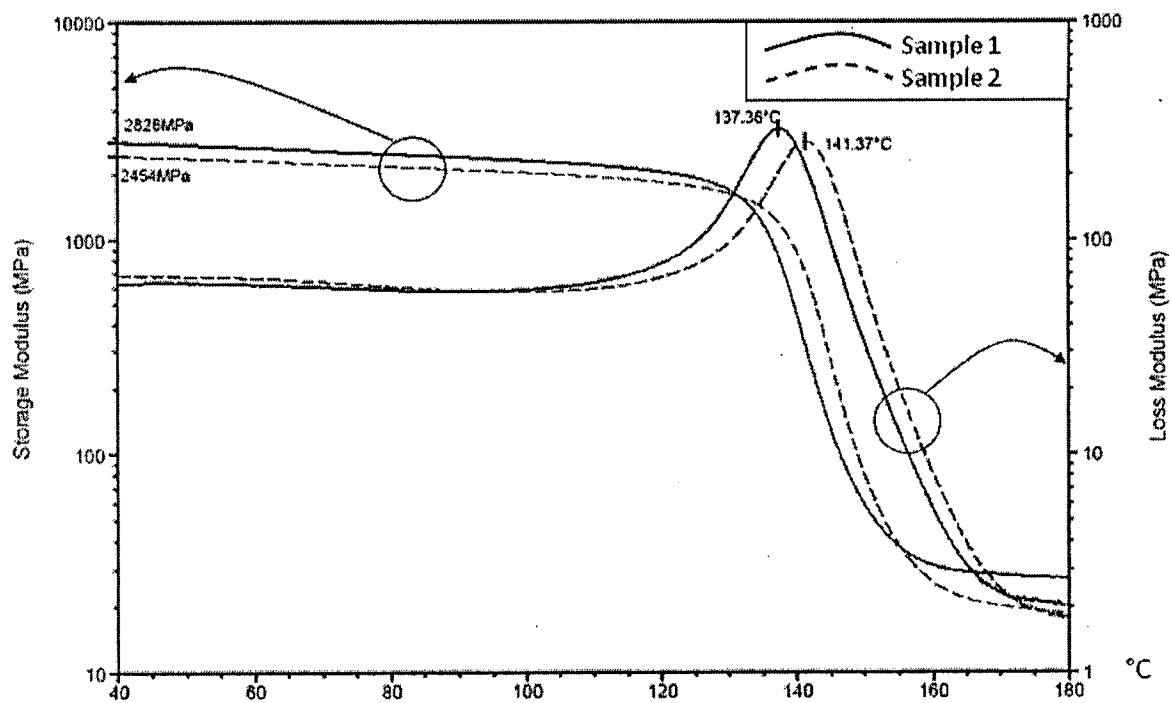


FIGURE 9B

18 / 19



FIGURE 10

19 / 19

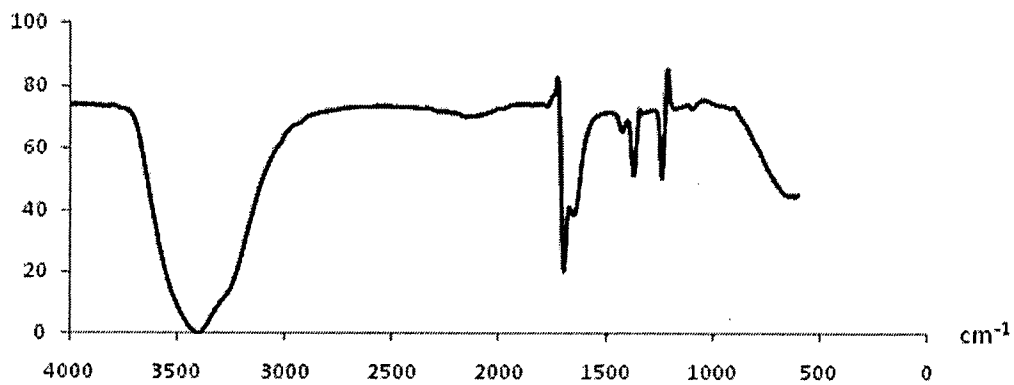


FIGURE 11A

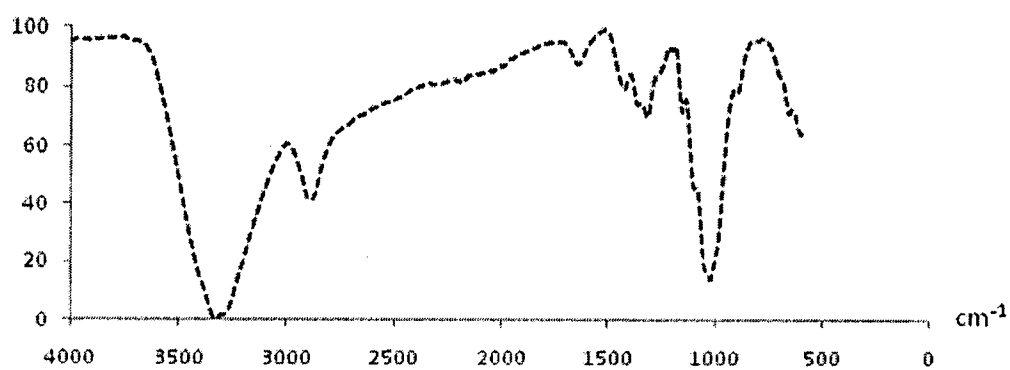


FIGURE 11B

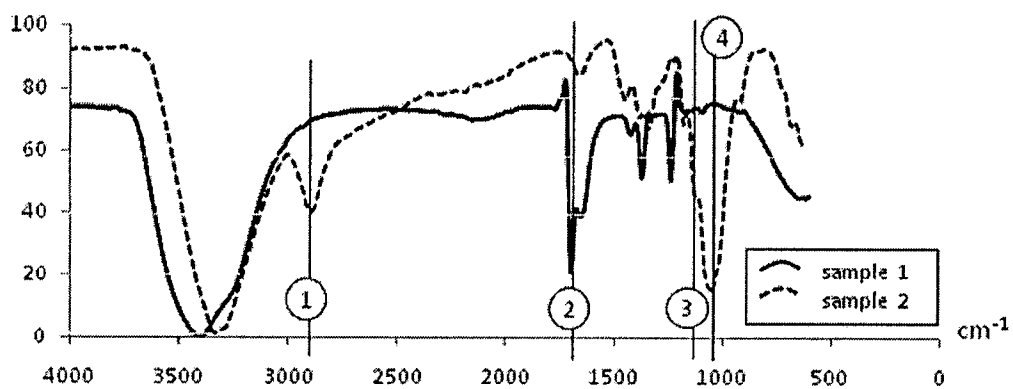


FIGURE 11C

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2014/000076

A. CLASSIFICATION OF SUBJECT MATTER
 IPC: **D21C 1/04** (2006.01), **B29C 70/06** (2006.01), **D21C 3/00** (2006.01), **D21C 5/00** (2006.01),
D21C 9/00 (2006.01), **D21H 11/02** (2006.01)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC: **D21C** (2006.01), **B29C** (2006.01), **D21H** (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
 Total Patent and Canadian Patent Database; cellulose, hemicellulose, lignin, ion, cation, anion, exotherm!; hydrochloric, nitric, acetic, phosphoric, p-toluensulfoninc, amine, phosphine, aminoethanol, iminodiethanol, nitirloethanol, compounds in claim 28, X-Ray, FTIR

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 336 291 (KIM et al) 22 June 2011 (22-06-2011) (* pages 4-9 *)	1-18, 20-22, 26, 29-32, 45
X	Park et al, <u>Biotechnology for Biofuels</u> , 2010, 3:10 24 May 2010 (24-05-2010) (* pages 2 and 3 *)	37,39 and 44
X	Perez et al "Conformation, Structure and Morphology of Cellulose" in <i>Polysaccharides: Structural diversity and functional variability</i> " 2 nd Edition, Marcel Dekker, 2005 (* Section X subsection C *)	41, 42 and 44
X	Åkerholm et al, Carbohydrate Research, 339, pp 569-578, 2004 (* Whole document *)	33 and 34
X	JP 2008-297364 (KAZUO et al) 11 December 2008 (11-12-2008) (* paragraph 12 and examples *)	46-49

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search
 03 April 2014 (03-04-2014)

Date of mailing of the international search report
 01 May 2014 (01-05-2014)

Name and mailing address of the ISA/CA
 Canadian Intellectual Property Office
 Place du Portage I, C114 - 1st Floor, Box PCT
 50 Victoria Street
 Gatineau, Quebec K1A 0C9
 Facsimile No.: 001-819-953-2476

Authorized officer

 Chris Bowen (819) 994-3555

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2014/000076**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Claims 1-32 and 45 are directed a process for producing a cellulose pulp and a product of that process.

Claims 33-48 are directed to an isolated cellulose material having certain features and properties and to a composite material using an isolated cellulose.

Claim 49 is directed to a composite material comprising a cellulose material and a resin or hardener.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CA2014/000076

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
EP2336291A1	22 June 2011 (22-06-2011)	EP2336291A1 KR20110067992A US2011143412A1	22 June 2011 (22-06-2011) 22 June 2011 (22-06-2011) 16 June 2011 (16-06-2011)
JP2008297364A	11 December 2008 (11-12-2008)	JP2008297364A JP5030667B2	11 December 2008 (11-12-2008) 19 September 2012 (19-09-2012)
—			