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(54) Title: METHOD AND DEVICE FOR PRODUCING DRY MICROFIBRILLATED CELLULOSE

(57) Abstract: The present invention provides a method for the drying of microfibrillated cellulose wherein a liquid suspension of cellulose fibres and a liquid carbon dioxide miscible liquid is formed and the liquid suspension is defibrillated. The liquid carbon dioxide miscible liquid is replaced by liquid carbon dioxide under pressure, and the carbon dioxide is removed by evaporation. A device for use therefore is also described.



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Method and device for producing dry microfibrillated cellulose

Technical Field of the Invention

5 The present invention relates to a method and a device for producing dry microfibrillated cellulose in a cost efficient and environmentally friendly way. The dry microfibrillated cellulose produced can be reconstituted without significant loss of important properties, in particular without significant loss of surface area, viscosity and gel-like structure relative to microfibrillated cellulose that has not been dried.

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Background of the Invention

Microfibrillated cellulose, hereinafter denoted MFC, is a valuable product derived from cellulose and is commonly manufactured in a process in which cellulose fibres in water are disintegrated to form microfibrils and/or nanofibrils by passage through a geometrical
15 constraint, such as in a homogenizer. The resulting gel-like, cellulose fibril aqueous slurry is used as such, or provided in a desired solvent, or dried. The common methods of drying are oven drying and freeze drying.

MFC has unique properties and leads to important commercial products that are utilized in a
20 wide range of industrial applications such as specialty paper manufacturing, composites, additives in the food industry, galenics and formulations in the pharmaceutical industry and in cosmetics applications, among others.

In order to be valuable to customers, the MFC should preferably be provided as a dried gel
25 or as a dry powder.

Manufacturing of dry MFC is usually avoided because the MFC quality, especially the properties derived from a large surface area, will deteriorate. MFC obtained according to US patent 4483743 (Turbak) is preferably used in un-dried form. To provide MFC in a desired
30 solvent other than water, solvent exchange of aqueous MFC is exemplified in US patent 6703497 (Ladouce), where solvent exchange is a part in the production of surface modified MFC. The solvents used were acetone, methanol and toluene, and the solvent exchanges were repeatedly done in a centrifuge or on a filter. No final drying of the solvent exchanged MFC is mentioned.

Oven drying is the most common drying concept both in laboratory and industrial preparation of cellulosic materials. When aqueous MFC is dried in an oven at e.g. 105°C, the fibrils stick irreversible to each other and form e.g. paper. The fibrils are thereafter difficult to disintegrate and important properties like the high surface area, e.g. as measured according to the BET method (Brunauer-Emmet-Teller method for the determination of the surface area, usually measured as area per weight unit), of the MFC is lost.

Another method for drying a composition comprising "fragile" solid substances (i.e. substances that are susceptible to heat or mechanical treatment), for example proteins or food ingredients, is freeze-drying the same. Therein, the term "freeze-drying" as generally understood, encompasses the sublimation drying of a deep-frozen composition. Typically the substance is solidified e.g. by freezing in a liquid medium. The liquid (such as water) is then removed in a vacuum below the triple point of the liquid. The vacuum is adjusted so that the frozen liquid turns directly into vapour in a sublimation process without first passing through the liquid stage. After the sublimation of the liquid, the solid remain, see e.g. US patent 4608764 (Leuenberger).

In any drying process involving frozen particles be it freeze-drying or otherwise, typically a large amount of (frozen) liquid must be removed effectively. Usually, a significant energy input is required to remove said liquid, for example by means of heating (evaporating the liquid) or by means of applying a vacuum (sublimating the liquid). While this may be feasible on a small scale, high costs for freezing and fine vacuum render this process prohibitive for commercial implementation in regard to effectively separating MFC from large amounts of liquid.

Freeze-drying of aqueous MFC slurry is common laboratory practice. However, in the drying operation, some important properties of the MFC may be lost. Also, impurities in the starting fibre pulp and process agents added in the homogenizing procedure are left in the dry MFC product. Furthermore, due to the costs of the process, freeze-drying of larger amounts of MFC is not an industrial feasible alternative.

It is an object with the present invention to reach to a method and a device for producing dry microfibrillated cellulose in a cost efficient and environmentally friendly way. The dry microfibrillated cellulose produced by the method should be reconstituted without significant

loss of properties, in particular without significant loss of surface area and properties derived from that, relative to a microfibrillated cellulose which has never been dried.

This object, and others, is/are addressed by a method and a device for producing MFC in dry form, in an industrially and commercially feasible and also environmental friendly way, by employing a method of solvent exchange and evaporation of the at least one liquid converted to gaseous form, and by a device for performing such operations.

Summary of the Invention

Accordingly, the present invention provides, in one aspect, a method for producing dry microfibrillated cellulose (MFC) and comprises at least the following steps:

- (i) providing a liquid suspension comprising a mixture of cellulose fibres in a liquid containing a carbon dioxide miscible liquid;
- (ii) subjecting the liquid suspension to high shear actions to form a MFC liquid suspension;
- (iii) displacing the liquid carbon dioxide miscible liquid in the MFC liquid suspension with liquid carbon dioxide under sub-critical conditions with regard to temperature and pressure;
- (iv) removing the liquid carbon dioxide by evaporation at about atmospheric pressure and a temperature above the boiling point of carbon dioxide to obtain dry MFC.

The present invention also relates to a device for drying microfibrillated cellulose (MFC), said device at least comprises:

- (a) means for providing a liquid suspension comprising a mixture of cellulose fibres in a liquid containing a carbon dioxide miscible liquid;
- (b) means for subjecting the liquid suspension to high shear;
- (c) means for exchanging the liquid carbon dioxide miscible liquid of the liquid suspension with liquid carbon dioxide at sub-critical conditions with regard to temperature and a pressure;
- (d) means for removing the liquid carbon dioxide from the MFC suspension by evaporation at about atmospheric pressure and a temperature above the boiling point of carbon dioxide.

Detailed Description of the Invention

The cellulose fibres employed as starting material in the process can be cellulose fibres from cellulose fibre sheets. Such cellulose fibre sheets are readily available from cellulose mills.

The cellulose fibre sheets are dried or partially dried cellulose obtained from a cellulose pulp.

5 For use as the starting material for the method of the invention, the fibre sheets are dissolved in a liquid containing a carbon dioxide miscible liquid, e.g. in ethanol. The liquid should consist mainly of the carbon dioxide miscible liquid, however, minor amounts of water (preferably less than 10%) and other products may be acceptable.

10 To facilitate the dissolution the fibre sheets may be shredded, and mixing e.g. by stirring of the fibre sheets and the liquid may be performed to facilitate the dissolution of the cellulose sheets. If stirring is performed, employing a mechanical stirring device is preferred. If necessary or desirable, water may be removed from the fibre sheet as explained for the cellulose pulp

15 Alternatively or additionally, the cellulose fibres are provided as a cellulose pulp. The cellulose pulp is usually in aqueous solution or dispersion, and can be prepared according to methods known in the art.

20 The cellulose pulp comprises a fibre material of paper, soft-wood and hardwood, fruit or vegetable origin, such as citrus, beets, orange or lemon or tomato, agricultural waste such as bagasse, and the like, or annual plants or energy crops, may be employed in step (i). These types of pulps are known in the art, and any mixture of these may also be used. Sulfite pulp is preferred, preferably that of soft-wood and in particular bleached sulfite pulp.

25 Hence, the starting material for the conversion of cellulose to MFC may be any cellulose fibres from a cellulose pulp, preferably a chemical pulp, further preferably bleached, half-bleached and unbleached sulphite, sulphate, soda pulps and Kraft pulps together with unbleached, half-bleached and bleached chemical pulps, and mixtures of these.

30 Said cellulose pulp may be mechanically or chemically or enzymatically pretreated or may not be pretreated at all.

A particularly preferred source of cellulose fibre is regular, fibre-length cellulose fibre sheets
35 and cellulose pulp, where the pulp is derived from either hardwood or soft-wood, or both types (in mixtures), normally available from a pulping operation, or pre-cut if desired.

Preferably, said pulp contains pulp from soft-wood. The pulp may also contain soft-wood of one kind only or a mixture of different soft-wood types. For example, said pulp may contain a mixture of pine and spruce or spruce only.

- 5 Evidently the water of the cellulose pulp usually will contain various other materials and chemicals from the pulping process, usually in dissolved form. Water in the context of the present invention means pure water and water comprising various other such materials and chemicals.
- 10 Liquid carbon dioxide miscible liquids which are feasible for the method according to the present invention should preferably be environmental friendly and non-toxic or having low toxicity, and being available in good supply and reasonably priced. Preferably, the liquids should also be water-soluble. Preferred liquid carbon dioxide miscible liquids comprise aliphatic alcohols, acetone and amyl acetate, butyl aldehyde and isobutyraldehyde. Lower
- 15 aliphatic alcohols are particularly preferred, especially methanol, ethanol, propanol and butanol and in particular ethanol. Acetone is also preferred as the liquid carbon dioxide miscible liquid. Mixtures of these liquids are also feasible. It is usually tolerable that the liquid carbon miscible liquid contains minor amounts of other compounds, in particular that it contains water, preferably in amounts of less than 10%.
- 20
- The concentration of the cellulose fibres in the liquid suspension of fibres and the liquid containing the carbon dioxide miscible liquid of step (i) of the process may vary. Preferably, the concentration of cellulose fibres in the liquid suspension of fibres and the liquid carbon dioxide miscible liquid amounts to a consistency of from approximately 0.5% to
- 25 approximately 5%, preferably about 1 to 3%, e.g. about 2%. By cellulose fibre consistency is meant the percentage of the cellulose fibres in the suspension comprising the fibres in the solvent, i.e. the solution or suspension.
- When employing cellulose fibres contained in a cellulose pulp, it may be favourable or necessary to adjust the proportion of water and fibres prior to performing process step (i).
- 30 Hence, in a preferred embodiment, an additional process step, step (0) may optionally be performed prior to step (i). Step (0) comprises
- (0) adjusting the cellulose fibre content of a cellulose pulp to an increased content of cellulose fibres, preferably to a consistency of from approximately 2% to approximately 10 % by the removal of water;

A wash press or a wash filter or similar equipment may be used, as well as other methods known from the state of art and used for this purpose in pulp mills.

A major part of the water of the cellulose fibre sheet or the cellulose pulp of the starting material is to be exchanged with the liquid carbon dioxide miscible liquid. Hence, more than 50% of the water by weight relative to the overall weight of water of the cellulose pulp should be exchanged, preferably, at least 80% or at least 90%, further preferably at least 95%.

"Microfibrillated cellulose" (MFC) in the context of the present invention is any material based on or comprising cellulose fibres that have been reduced in their size to result in microfibrils and/or nanofibrils.

The process step (ii) of subjecting the cellulose pulp to high shear actions to form the MFC liquid suspension is well known from the art.

A homogenizing process performed by the passing of a liquid suspension of cellulose fibres through a small-diameter orifice in which the suspension is subjected to high-velocity shearing actions is a useful method for the forming of cellulose micro and nano fibrils of the MFC. Such MFC is known from the art, for example from US patent 4374702 (Turbak). According to Turbak, microfibrillated cellulose has properties distinguishable from celluloses known previously and is produced by passing a liquid suspension of cellulose through a small diameter orifice in which the composition is subjected to a pressure drop of at least 3000 psig and a high velocity shearing action followed by a high velocity decelerating impact. The passage of said composition through said orifice is repeated until the cellulose composition becomes a substantially stable composition. This process converts the cellulose into microfibrillated cellulose (MFC) without substantial chemical change of the cellulose starting material

Further, WO 2007/091942 of STFI-Packforsk AB (STFI) describes a method for treatment of chemical pulp for the manufacturing of microfibrillated cellulose comprising the following steps: a) providing a hemicellulose containing pulp, b) refining said pulp in at least one step and treating said pulp with one or more wood degrading enzymes at a relatively low enzyme dosage, and c) homogenizing said pulp thus providing said microfibrillated cellulose.

Another process for manufacturing microfibrillated cellulose (MFC) is described in US 5 385 640 (Weibel). Weibel provides relatively simple and inexpensive means for refining

fibrous cellulosic material into a dispersed tertiary level of structure and thereby achieving the desirable properties attendant with such structural change. The cellulosic fibre produced in this way is referred to as "microdenominated cellulose (MDC)", a sub-group of microfibrillated cellulose. Microfibrillated cellulose is therein obtained by repeatedly passing a liquid composition of fibrous cellulose through a zone of high shear, which is defined by two opposed surfaces, with one of the surfaces rotating relative to the other (rotor/stator device), under conditions and for a length of time sufficient to render the composition substantially stable, and to impart to the composition a water retention that shows consistent increase with repeated passage of the cellulose composition through the zone of high shear.

Most preferred is the homogenization process. In using a liquid carbon miscible liquid according to the present invention, e.g. ethanol or acetone, as part of the liquid of the cellulose suspension to be defibrillated, the exchange of the liquid carbon dioxide miscible liquid with liquid carbon dioxide will be facilitated. If necessary, lubricants may be used during the homogenization procedure. An example of such a lubricant is PEG (polyethylene glycol).

The MFC composition is obtained from a homogenizer as a gel or as a high viscosity composition typically having a consistency of less than about 5% and in some instances significantly less than 5%, for example less than 3% or less than 2% or about 1% to 0,5%.

The liquid carbon dioxide miscible liquid of the MFC liquid suspension is displaced to the desired degree by liquid carbon dioxide by methods known from the state of art such as exchanging repeatedly the liquid in the MFC suspension with liquid carbon dioxide under pressure. The pressure and the temperature are in the subcritical region. When operating in the carbon dioxide liquid region, the temperature must be beyond the boiling point of carbon dioxide at the employed pressure. In the interest of optimizing the economy of the process, the ratio of the pressure and the temperature should be balanced. Preferably the pressure should be relatively low and may vary between approximately 10 and 70 bar, while the temperature should be from minus 55°C to 31°C. At ambient temperature, a pressure of about 40 bars may be employed. The displacement of the liquid carbon dioxide miscible liquid by liquid carbon dioxide may take place in a number of conceivable ways. Preferably the displacement is performed in a container that can be pressurized, preferably a container that can also be exerted to movements during the procedure, e.g. which can be shaken and/or rotated. The movements of the container during the displacement will avoid the

formation of big particles. The movements of the container should be adjusted to provide dried MFC particles of the desired size. Usually, particles appearing as a powder are desired.

In a particularly preferred embodiment, a rotating drum, e.g. a washing drum, can be used in the process. The MFC liquid suspension may be loaded into a perforated container which is placed in the washing drum. The washing drum can be rotated around any axis, e.g. a horizontal axis or a vertical axis, preferably around a substantially horizontal axis. The rotation may be in one direction only or may change direction during time, e.g. in an agitational manner as is usual for commercial available washing drums. Suitable perforated containers may be of almost any form and material and may simply be a washing bag for domestic use.

The liquid carbon dioxide miscible liquid together with a fraction of the liquid carbon dioxide is removed to a separator vessel, continuously or batch-wise during the displacement process. In a separator, the carbon dioxide is decompressed and returned to a gaseous state, preferably for reuse. The liquid carbon dioxide miscible liquid together with any contaminants or other additives or liquids present will remain in the liquid form and are removed from the separator vessel, e.g. through a bottom valve. The liquids may preferably be refined for reuse.

The gaseous carbon dioxide is sent through a cooling device, pressurized and returned to the container e.g. the washing drum, optionally via a storage tank.

During the repeated displacement process, the removed liquid mixture contains increasing amounts of liquid carbon dioxide. When the mixture of liquids in the mixture of liquids and fibres in the container is brought down to the amounts of liquids acceptable for the dry product, the displacement procedure is discontinued.

It may be advantageous to add detergents, surfactants, enzymes or other additives desired in the further processing of the MFC to the liquid carbon dioxide.

At the end of the drying process, when substantially all the liquid carbon dioxide miscible liquid is removed from the MFC containing material, the carbon dioxide is removed, preferably by evaporation. Hence, the pressure in the container, e.g. the washing drum, is released to allow the carbon dioxide to evaporate in gaseous form. This may simply be done by opening the pressurized container to the atmosphere to decrease the pressure to

approximately atmospheric pressure. More preferred the pressure is decreased by opening a valve in a pipe leading to a holding container maintaining a lower pressure, e.g. about atmospheric pressure, to allow the carbon dioxide to be collected for reuse as explained above.

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In the context of the present invention, "dried" and "dry" microfibrillated cellulose (MFC) and "drying" microfibrillated cellulose (MFC) means removing at least some liquid from the MFC liquid suspension produced in step (ii), which is a composition comprising MFC in a liquid, often comprising a fraction of water. In the final product, the dry MFC, as much as 50% by weight relative to the overall weight of the final product may remain as liquid. Preferably, not more than 20% or more that 10%, further preferably not more than 5%, should remain as liquid, wherein liquid in this context mainly comprises water. Most preferably, at the end of the drying process, in accordance with the present invention, the MFC is present as an essentially dry powder or solid.

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In a preferred embodiment, the method for producing dry MFC comprises the following steps and features:

- (0) optionally adjusting the cellulose fibre content of a cellulose pulp to a consistency of from approximately 2% to approximately 10 % by the removal of water;
- (i) preparing a liquid suspension of cellulose fibres in a solvent containing a liquid mainly comprising a carbon dioxide miscible liquid, preferably ethanol,
- (ii) homogenizing the liquid suspension of cellulose fibres to form a MFC liquid suspension;
- (iii) displacing the liquid carbon dioxide miscible liquid in the MFC liquid suspension with liquid carbon dioxide under a pressure of from approximately 10 to approximately 70 bar and a temperature of from minus 55°C to 31°C, preferably to about 40 bar at about ambient temperature;
- (iv) decreasing the pressure to about atmospheric pressure and about ambient temperature to evaporate the carbon dioxide to obtain dry MFC

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In another embodiment, the present invention relates to a device for the drying of microfibrillated cellulose (MFC), said device at least comprising:

- (a) means for providing a liquid suspension comprising a mixture of cellulose fibres in a liquid containing a carbon dioxide miscible liquid

(b) means for subjecting the liquid suspension to high shear;

(c) means for exchanging the liquid carbon dioxide miscible liquid of the liquid suspension with liquid carbon dioxide under sub-critical conditions with regard to temperature and pressure;

5 d) means for removing the liquid carbon dioxide mixture from the MFC suspension by evaporation at about atmospheric pressure and at a temperature above the boiling point of carbon dioxide.

10 The means (a) may be a container or similar suitable for dissolving fibre sheets in the desired liquid and/or for a solvent exchange, e.g. by adding the liquid carbon dioxide miscible liquid to the cellulose pulp and draining off water and liquid usually in repeated steps. In order to regulate the cellulose fibre consistency of the cellulose pulp starting material, the device may contain means for the removal of water from the pulp. As explained above, such means may be a wash press or a wash filter or similar equipment as well as similar equipment known
15 from the state of art and used for this purpose in pulp mills.

The means (b) for subjecting the liquid suspension to high shear forces may be a homogenizer or a rotor/stator equipment or similar as known from the state of art and as discussed above.
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Furthermore, means (c) for exchanging liquid carbon dioxide miscible liquid with liquid carbon dioxide may be a moveable container or similar as is also discussed above, in particular a rotating washing drum.

25 Means (d) for the removal of the liquid carbon dioxide mixture from the MFC suspension may simply be a valve for releasing of the pressure to the environment or through a pipe to a holding container as is further described.

30 The liquid carbon dioxide miscible liquid and the liquid and gaseous carbon dioxide are preferably recovered and reused. Hence, the device preferably includes means (c'), a holding container, for collecting the liquid carbon dioxide miscible liquid and liquid carbon dioxide which are released during the steps of the process.

Means for the collection of the liquid carbon dioxide miscible liquid, which many also contain
35 water and/or materials and chemicals from the pulping process, may be any suitable device

such as a tank. The collected liquid can be separated in its different constituents and recirculated as desired.

Likewise, the liquid carbon dioxide released during the process steps together with the liquid carbon dioxide miscible liquid should be collected and decompressed to carbon dioxide gas in a separator maintaining a lower pressure, e.g. about atmospheric pressure, to allow the carbon dioxide to be collected and processed for reuse as carbon dioxide in its liquid state as explained above.

The dry MFC produced by the method of the invention is found to have several desired properties which make the MFC particularly useful for the commercial purposes mentioned above, in particular for the use in composites, additives in the food industry, galenics and formulation in the pharmaceutical industry and in cosmetics applications, among others. In particular, it is found that the surface area of the dried MFC is particularly high, possibly because the surface tension between the different micro and/or nano fibrils is reduced. The dried MFC will also have a low bacteria number, in particular when bactericides such as ethanol are used during the process. The treatment with liquid carbon dioxide under enhanced pressure also has a positive effect to reduce the bacteria load in the dried MFC. Usually also, none of the additives frequently used in the preparation of dried MFC is needed.

Hence, the dried MFC obtained by the present method has several highly desired properties sought by the industry.

Said dried MFC, in particular if present as a powder or a solid, may be reconstituted by means of adding the same or any other liquid or liquid mixture, if necessary while employing shear forces and/or means of mixing.

The composition comprising MFC before drying and after reconstitution in at least one liquid, in particular water, may have a dynamic viscosity that is 10 times or 100 times or 1000 times higher than the viscosity of water. Said composition may in particular be present as gel. As an aqueous dispersion or suspension, MFC preferably has non-Newtonian flow properties, for example displaying shear thinning and a gel-like consistency.

Documents cited above are hereby included by reference.

Examples

The units of measurement are metric units if not noted otherwise.

Example 1

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Bleached sulfite pulp from spruce, SR 90 (Schopper Riegler, a standard method for the measurement of the degree of defibrillation in paper industry), consistency 30 % (weight of fibres/weight of solution), is diluted with industrial ethanol, mixed and centrifugated to 30 % consistency. The dilution and centrifugation was repeated once. The ethanol pulp slurry was then diluted with ethanol to a consistency of 2%. Polyethyleneglycol (10% by weight of the weight of the fibres) was mixed in and the slurry was homogenized by passing the slurry through a 100 micron orifice at a pressure of 2000 bar. 10 volume% of the ethanol was drained off the MFC on a filter. The resulting MFC slurry (4 l) was put in a net bag and the bag was put into a drum of a CO₂ textile dry cleaning machine. The air was evacuated; the drum pressurized to 40 bars; and liquid carbon dioxide added (100 l). The drum started to rotate and after 10 min., the washing liquid was drained off and a new portion of 100 l of liquid carbon dioxide was added. This was repeated two more times, after which the pressure was released and the net bag with the dry MFC (70 % weight of fibres) was taken out of the washing machine.

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Example 2

Bleached sulfite pulp from spruce, SR 90 (Schopper Riegler, a standard method for the measurement of the degree of defibrillation in paper industry), consistency 30 % (weight of fibres/weight of solution), is air-dried at room temperature to 95 % dryness and then diluted with industrial ethanol containing less than 1 % water to a consistency of 1,5%. The fibre/ethanol slurry was mixed with an Ultrathurax mixer until most of the fibers were free-floating. The mixed fibre/ethanol slurry was homogenized twice by passing the slurry through a 200 micron orifice at a pressure of 2000 bar. 10 volume% of the ethanol was drained off the MFC on a filter. The resulting MFC slurry was put in a net bag and the bag was put into a drum of a CO₂ textile dry cleaning machine. The air was evacuated; the drum pressurized to 40 bars; and liquid carbon dioxide added (70 l). The drum started to rotate and after 10 min., the washing liquid was drained off and a new portion of 70 l of liquid carbon dioxide was added. This was repeated six more times, after which the pressure was released and the net bag with the dry MFC was taken out of the washing machine. The dryness of the MFC was

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95 % and the surface area (BET) was 20 m²/g. This BET value is at the same level as the water diluted reference sample, which was more extensively homogenized by passing through a 100 micron orifice and then freeze dried.

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Claims

1. Method for producing dry microfibrillated cellulose (MFC) comprising at least the following steps:

- 5 (i) providing a liquid suspension comprising a mixture of cellulose fibres in a liquid containing a carbon dioxide miscible liquid;
- (ii) subjecting the liquid suspension to high shear actions to form a MFC liquid suspension;
- (iii) displacing the liquid carbon dioxide miscible liquid in the MFC liquid suspension
10 with liquid carbon dioxide under sub-critical conditions with regard to temperature and pressure;
- (iv) removing the liquid carbon dioxide by evaporation at about atmospheric pressure and a temperature above the boiling point of carbon dioxide to obtain dry MFC.

15 2. Method of claim 1 wherein the liquid suspension of cellulose fibres is obtained by replacing a major part of the water in a cellulose pulp with a liquid containing a carbon dioxide miscible liquid.

20 3. Method of claim 1 wherein the liquid suspension of cellulose fibres is obtained by suspending dried cellulose fibres in a liquid containing a carbon dioxide miscible liquid.

25 4. Method of claims 1 to 3 wherein the cellulose fibres are obtained from paper, soft-wood and hardwood, fruit or from vegetable origin, such as citrus, beets, orange or lemon or tomato pulp, agricultural waste such as bagasse, or annual plants or energy crops.

5. Method of claim 4 wherein the cellulose fibres are obtained from sulphite pulp of soft-wood and in particular bleached sulphite pulp.

30 6. Method of the preceding claims wherein the liquid carbon dioxide miscible liquid comprises aliphatic alcohols, acetone, amyl acetate, n-butyl aldehyde and isobutyraldehyde and mixtures thereof.

7. Method of claim 6 wherein the liquid carbon dioxide miscible liquid comprises lower aliphatic alcohols such as methanol, ethanol, propanol and butanol and in particular ethanol.

8. Method of claims 1, 2 and 4 to 7 wherein at least 50% by weight of the water in the cellulose pulp is replaced by a liquid carbon dioxide miscible liquid.

9. Method of the preceding claims wherein concentration of cellulose fibres in the liquid suspension comprising the fibres and the liquid containing carbon dioxide miscible liquid amounts to a consistency of from approximately 0.5% to approximately 5%.

10. Method of claims 1 to 2 and 4 to 9 wherein prior to step (i) a step (0) is performed comprising adjusting the cellulose fibre content of a cellulose pulp to an increased content of cellulose fibres, preferably to a cellulose fibre consistency of from approximately 2% to approximately 10 %, by the removal of water.

11. Method of the preceding claims wherein the high shear action of step (ii) is provided by a homogenization process and wherein the MFC liquid suspension has a consistency of less than about 5% of cellulose fibres.

12. Method of the preceding claims wherein the liquid carbon dioxide miscible liquid in the MFC liquid suspension is displaced with liquid carbon dioxide under a pressure of from approximately 10 to approximately 70 bar and a temperature of from minus 55°C to 31°C.

13. Method of the preceding claims wherein the liquid carbon dioxide is removed by decreasing the pressure to about atmospheric pressure and evaporating the carbon dioxide at a temperature above the boiling point of carbon dioxide.

14. Method of the preceding claims wherein the displacement of the liquid carbon dioxide miscible liquid with liquid carbon dioxide and the removal of the liquid carbon dioxide are repeated until the MFC has reached the desired dryness.

15. Method of claim 14 wherein the dry MFC contains equal or less than 50% by weight of liquid relative to the overall weight of the final product.

16. Method of claim 15 wherein the dry MFC contains not more than 20%, preferably not more than 10%, further preferably not more than 5% of a liquid.

17. Method of claim 15 wherein the dry MFC in the form of essentially dry powder or solid.

18. Method of claims 15 to 17 wherein the liquid essentially comprises water.

5 19. Device for producing dry microfibrillated cellulose (MFC) of claims 1 to 18 comprising

(a) means for providing a liquid suspension comprising a mixture of cellulose fibres in a liquid containing a carbon dioxide miscible liquid; (b) means for subjecting the liquid suspension to high shear;

10 (c) means for exchanging the liquid carbon dioxide miscible liquid of the liquid suspension with liquid carbon dioxide at sub-critical conditions with regard to temperature and pressure;

d) means for removing the liquid carbon dioxide from the MFC suspension by evaporation at about atmospheric pressure and at a temperature above the boiling point of carbon dioxide.

15 20. Device of claim 19 wherein means (b) comprises a homogenizer.

21. Device of claim 19 and 20 wherein means (c) comprises a container that can be pressurized and be exerted to movements such as shaking and/or rotation, preferably a rotating drum.

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22. Device of claims 19 to 21 wherein means (d) comprises means for collection of the carbon dioxide and/or the liquid carbon dioxide miscible liquid, preferably for collection and reuse.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/000489

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21C9/00 D21D1/20 D21D1/34
ADD. D21H11/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D21C D21D D21B

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 538 257 A1 (JAPAN ABSORBENT TECH INST [JP]) 8 June 2005 (2005-06-08) paragraph [0023]; claims 1-15 -----	1-22
A	US 6 183 596 B1 (MATSUDA YUJI [JP] ET AL) 6 February 2001 (2001-02-06) column 7, line 62 - column 8, line 14 -----	1-22
A	US 4 483 743 A (TURBAK ALBIN F [US] ET AL) 20 November 1984 (1984-11-20) claims 1-10; example 11 -----	1-22
A	US 6 703 497 B1 (LADOUCE LAURENCE [FR] ET AL) 9 March 2004 (2004-03-09) cited in the application example 1 column 4, line 38 - line 55 ----- -/-	1-22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

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"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
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"&" document member of the same patent family

Date of the actual completion of the international search

25 May 2011

Date of mailing of the international search report

20/06/2011

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/000489

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A,P	EP 2 226 171 A1 (MITSUBISHI CHEM CORP [JP]) 8 September 2010 (2010-09-08) claims 9-12 paragraphs [0116], [0117] -----	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/000489

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