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(54) Title: METHOD AND INTERMEDIATE FOR THE PRODUCTION OF HIGHLY REFINED OR MICROFIBRILLATED CELLULOSE

(57) Abstract: The invention concerns a method for the production of highly refined or micro-fibrillated cellulose (MFC), comprising the steps of treating cellulosic fibres to remove at least a major part of the primary wall of the fibres, drying the treated fibres, re-wetting the treated fibres, and disintegrating the wetted fibres by mechanical means to obtain the final product. The invention further concerns dried cellulosic pulp as an intermediate product of the method, having an average fibre length of at least 0.4 mm, while less than 50 % of the primary wall material of natural untreated fibres is left in the intermediate product. Instead of transporting large amounts of dilute MFC dispersion the invention enables transport of the dry intermediate product to the MFC end user, who would complete the process by turning the intermediate product to final MFC by use of standard disintegrating devices.



## **Method and intermediate for the production of highly refined or microfibrillated cellulose**

### **Field of the invention**

- 5 The invention relates to a method for the production of highly refined or microfibrillated cellulose. Furthermore, the invention covers a dried cellulosic pulp, which is obtainable as an intermediate product of said method, a method for the production of said intermediate, as well as use of said intermediate.

### **Background of the invention**

- 10 Microfibrillated cellulose (MFC) is fibrous material comprised of cellulosic fibres, which are very thin, of a diameter of about 5 to 100 nm, in average about 20 nm, and have a fibre length of about 100 nm to 10  $\mu\text{m}$ . Nanofibrillated cellulose (NFC) is a specific class of MFC with fibre dimensions at the low end of said fibre size range. MFC has a very large open active surface area, generally  
15 in the range of about 1 to 100  $\text{m}^2/\text{g}$ , and is useful for a wide range of end used, notably in the field of papermaking.

- Various known methods of microfibrillation of cellulosic fibres are summarized in US 6,602,994 B1 as including e.g. homogenization, steam explosion, pressurization-depressurization, impact, grinding, ultrasound, microwave explosion,  
20 milling and combinations of these. Passing non-microfibrillar polysaccharide through a homogenizer at least three times is the preferred method according to this reference.

- WO 2007/001229 adds to the above list enzyme treatment and, as a method of choice, oxidation in the presence of a transition metal for turning cellulosic  
25 fibres to MFC. After the oxidation step the material is taught to be disintegrated by mechanical means.

- In most cases MFC is produced in an aqueous phase, and high quality MFC is produced typically as a slurry having a solid content of 1.5 to 2.5 %. Due to the high open surface area and the high water bonding ability of MFC the viscosity  
30 of slurries of such low solid contents is already very high.

The low solids content makes delivery of MFC to customers uneconomical due to the large volumes being transported. This is one of the limiting factors in industrial MFC usage in large quantities. Furthermore, there are several applications where a high water content as such is a problem, for example manufacture of composites with plastics, asphalt, tires etc., as well as pillerizing.

An approach to solving the transport and high water content problems is drying the MFC product for the transport and rewetting or redispersing it at the end user. A problem of this procedure is a tendency for irreversible agglomeration (hornification) of the fibres in connection with drying, which would hamper subsequent redispersion of the same. Hornification can occur during drying of aqueous NFC suspensions or during compounding of NFC with hydrophobic polymers and it can be explained with the formation of a large number of hydrogen bonds between the hydroxyl groups of adjacent fibrils. This process is accompanied by a considerable decrease of the NFC aspect ratio and consequently results in the complete loss of its beneficial properties.

US 4,481,076 teaches preparation of redispersible MFC by addition of substances capable of inhibiting hydrogen bonding between cellulose fibrils and then drying the product. In this way hornification would be avoided and regaining a high surface area would be secured, but the additives increase the cost of the product, and their presence may be harmful for various end uses of the product.

With an aim to reduce the amount of additives US 6,231,657 B1 teaches preparation of NFC predominantly from primary walls of cellulosic fibres. Such NFC would be easily dispersible to an aqueous medium.

Water-redispersible NFC may be prepared in powder form e.g. by carboxymethylation and mechanical disintegration of refined, bleached chemical pulp. The powders will form stable gels when dispersed in water. Thus by carboxymethylation hornification of NFC can be successfully prevented during drying. The chemical modification of cellulose as required is expensive, however, and in some applications such modification is not accepted.

It is also known to dry MFC via solvent exchange and thus partially prevent hornification and fiber-to-fiber bonds. This way it is possible to regain high open surface area and bonding ability of the MFC when rewetted.

As MFC is comprised of very fine material there is also a considerable risk of dusting and the ensuing safety of handling problem. Drying of MFC due to its high open surface is also much more difficult than drying of ordinary cellulose fibres and required specialized equipment differing from that used for ordinary pulp drying. Dusting then is a handicap not only in drying but as well in re-wetting at the end user's facilities.

An alternative approach of avoiding the transport problem would be to remove the entire MFC preparation process to be carried out by the end user. This would be highly costly and impractical, however, losing the benefits of large-scale production at a specialized factory. The pulp milling or disintegration steps are relatively simple and conceivably could be carried out at pulp mills, but the more demanding preparatory steps would destroy the overall economy of this approach.

There is thus a need for new more energy and cost efficient solutions for delivering MFC to end users, avoiding chemical modification and additives and allowing deliveries in a more simple and safe way.

### **Summary of the invention**

(a) The invention has the purpose of providing a solution to the above problem, which satisfies the requirements of reducing the bulk of material being transported to the end user of MFC or NFC, maintaining the cost benefits of mass production, and providing a product, which is manageable for the end user without need of specialized equipment and procedures to obtain wetted or dispersed fibres. The solution according to the invention is a process for the production of highly refined or microfibrillated cellulose, which comprises the steps of: (a) treating cellulosic fibres to remove at least a major part of the primary wall of the fibres, (b) drying the treated fibres, (c) rewetting the treated fibres, and (d) disintegrating the wetted fibres by mechanical means to obtain the final product.

The concept of the invention bringing its benefits is to have the more demanding preparatory steps (a) and (b) of the above process carried out at a specialized plant, then transport the dry intermediate product of step (b) to the end user, and finally having the end user to turn the intermediate product to the final MFC or NFC according to less demanding steps (c) and (d).

According to the finding of the present inventors by removing primary wall of the pulp fibres it is possible to produce material that can be turned to MFC or NFC without difficulty. Surprisingly this property, that is, suitability to MFC or NFC production, is preserved as the fibres are dried, as opposed to the prior art teachings, which warn of heavy hornification of the dried fibers, thus making the fibers unsuitable for MFC production.

Thereby there is provided an economical route for the end user to acquire and utilize MFC or NFC without the need of investing in expensive fibre pretreatment equipment. Only an apparatus for mechanical disintegration of the dry intermediate product is needed.

Thus the preferred way of practicing the invention is that the fibres dried at step (b) are transported to be rewetted and disintegrated according to steps (c) and (d) at a different location. The fibres may be dried at step (b) to a water content of about 20 wt-% or less, suitably to about 15 wt-% or less.

There are different ways for the removal of the primary wall material at step (a). Such techniques include e.g. mechanical refining, oxidation, preferably by use of peroxide or ozone, enzymatic treatment, preferably by use of a cellulase enzyme, and mechanical defibrillation combined with oxidation and/or enzymatic treatment.

More specifically, the primary wall of the fibres can be removed by increasing the pre-treatment of the fibres. Thus, increased refining, preferable high consistency refining has been shown to be very effective. Also, oxidising chemicals (Tempo ext.) or enzymes affecting celluloses and/or hemicellulose can be used, either alone or in combination with refining, preferable high consistency refining. It has been shown that the combination of enzymatic pre-treatment or oxidising chemicals, mechanical pre-treatment, enzymatic treatment and a mechanical treatment is very effective when it comes to removing the primary walls of cellulosic fibres.

The cellulosic fibres used in the process according to the invention are preferable fibres of kraft pulp, i.e. they have been treated according to the kraft process. It has been shown that the primary wall of the fibres in kraft pulp often prevents the fibres from forming fibrils. However, removal of the primary wall according to the teachings of the invention turns kraft pulp very useful for making MFC or NFC.

Also other pulps can also be used, for example sulphite pulp or agro based fibres. Typically fibres with thin fibre walls are preferably used.

5 Due to increased initial wet strength it is possible to run the stock obtained at step (a) of the invention in a pulp drying machine even when the solids content after wire section and press section is relatively low. It is also possible to reduce grammage of the web without problems. The pulp is also suitable for utilization in drying machines, where high shrinkage and high tension stretch is needed.

10 The preferred way of producing the microfibrillated cellulose (MFC or NFC) at step (d) is by use of a homogenizer and a fluidizer in succession.

15 As the general concept and teaching of the invention is to refine cellulose at two consecutive disintegration steps (a) and (d), with drying (b) and then re-wetting (c) the fibres between said steps, the invention is not strictly limited to the production of MFC and NFC but also includes production of highly refined cellulose of slightly larger particle size, the fibers having a diameter up to 500 nm or more and a length of 500  $\mu\text{m}$  or more.

20 The intermediate product obtained at step (b) of the above-described process, which forms a part of the invention, is a dried cellulosic pulp having an average fibre length of at least 0.4 mm, while less than 50 % of the primary wall material of natural untreated fibres remains present in said product.

In the intermediate product the average fibre length may be more than 70 %, preferably more than 80 %, more preferably more than 90 % of the average fibre length of the untreated fibres the product has been made from.

25 Preferably the intermediate product has a content of at most 5 wt-% of fines with a fibre length less than 10  $\mu\text{m}$  and a water content of less than 20 wt-%.

Preferably the intermediate product has a Shoppler-Riegler (SR) drainage resistance, which is in the range of 20SR–50SR, preferably 20SR–40SR, and more preferably 20SR–35SR.

30 Preferably the intermediate product has a wet zero-span tensile strength, which is less than 60 Nm/g, preferably less than 50 Nm/g, and more preferably less than 40 Nm/g.

Preferably the intermediate product has a BET surface, which is more than 40 m<sup>2</sup>/g, preferably more than 60 m<sup>2</sup>/g.

The aim in the invention is to avoid additives that could harm the final uses of the MFC product. Preferably the content of any substances added to the intermediate product for improving redispersability of the same is less than 1 wt-%.

The dried intermediate product can be in the form of stacked sheets, suitable for the transport to a different location.

The method of producing the dried cellulosic pulp described as an intermediate in the above comprises (a) treating cellulosic fibres to remove at least a major part of the primary wall of the fibres, to obtain fibres with an average fibre length of at least 0.4 mm, and (b) drying the fibres obtained at step (a). The various embodiments of this method correspond to the embodiments involving steps (a) and (b) of the method of producing the highly refined or microfibrillated cellulose as described above.

Use of the dried cellulosic pulp described as an intermediate in the above comprises use for the production of highly refined or microfibrillated cellulose, through the steps of rewetting and disintegration by mechanical means. Preferably these final steps are carried out at a location different from the location where the intermediate is produced.

The invention is illustrated by means of the following examples, which are not to be construed as limiting the invention, however.

### Examples

Generally, as the starting material fibres of any kind of wood fibres, such as hardwood fibres or softwood fibres, and/or agricultural fibres may be used. The pretreatment can be mechanical treatment, such as disintegration, enzymatic treatment, carboxy methylation, TEMPO oxidation, CMC grafting, chemical swelling, acid hydrolysis or other methods which will facilitate the formation of microfibrillated cellulose. The pretreatment can be done in one or more steps.

For the tests bleached pine kraft pulp was chosen as the starting material. The pretreatment was enzymatic, and the intermediate product was dried with air or

in oven at 105 °C. The intermediate product was turned to final MFC dispersion product by disintegration and fluidization.

As comparative examples the same pine kraft pulp was used as wet (sample 1), dry (sample 2), and as pretreated but without being dried (sample 3). The  
5 examples according to the invention are the kraft pulp pretreated and air dried (sample 4) and the kraft pulp pretreated and oven dried.

For the pretreatment the wet bleached kraft pine pulp was mixed in a 5 m<sup>3</sup> pulper in a consistency of 3.5–4.5 %. The temperature of the pulp was adjusted to 50 °C, and the pH was adjusted to 5.

10 A 250 ECU dosage of Endoglucanase (EG) enzyme was added. Mixing was continued for 2.5 hours. After this the temperature was increased to 85 °C and pH adjusted to 10 in order to inactivate the enzyme. The enzymatically treated pulp was run through a pilot paper machine and dried as sheets with air to a moisture content of 37.2 %. Part of the sheets were torn into pieces and dried  
15 in an oven at 105 °C for 19 h.

The results of measurements carried out for the dried intermediate product according to the invention (samples 4 and 5) and the comparative materials (samples 1-3) are shown in Table 1.

The results show that the fibers have preserved over 85 % of their original fiber  
20 length in the pretreatment. Such pretreated and dried intermediate product is free of a dusting problem. At the same time especially the drastically reduced zero-span tensile strength show a major change having taken place in the fibres. The low values mean that the fibres will disintegrate easily as the material is turned to MFC at the final steps. The SR drainage resistance values have  
25 grown, but not too much to prevent effective drying of the fibres on a moving web. Standard evaporation drying methods and devices used for normal pulps may be used for the drying.

The procedure was then continued by storing the dried pulp sample (5) in a plastic bag for one month. After this the dried pulp was dispersed in water to  
30 form a dispersion of 3% solids content and immediately disintegrated with 30000 revolutions in a standard laboratory disintegrator. The mass of each batch of pulp was 1488 g during the disintegration.



Immediately after disintegration, the pulp was fluidized in a microfluidizer, with an interaction chamber with a dimension of 400  $\mu\text{m}$  and an auxiliary processing module with a hole dimension of 200  $\mu\text{m}$ .

5 The runnability of this pulp in a paper machine was only slightly worse than the never-dried pretreated pulp (sample 3) of the same type. No plugging problems, however, appeared.

10 An inspection of photos of MFC made from never-dried pretreated pulp and MFC made from dried pretreated pulp as described (samples 3 and 5, respectively) here showed very little visual difference, but the measured viscosity of an aqueous dispersion of the latter appeared to be smaller than that of the former.

15 A comparative test was performed with the non-pretreated dried pulp (sample 2). The original fibre length of 2.2 mm was first reduced to about half by use of a Wiley mill. An attempt to turn wetted fibres into a fibrous dispersion in the laboratory disintegrator failed. At low solids contents the fibres were not gelled, and at higher solid contents the material did not pass the device. In a 78/22 wt-% mixture with standard MFC the comparative milled pulp was runnable, but was then left unaffected by the fluidizer. The pretreatment required in the invention appears to be necessary for turning the starting material into MFC.

20

Table 1

Sample	1	2	3	4	5
Pulp properties	never dried pine (ref) wet ref.	dried pine (ref) dry reference	never dried treated	dried pre-treated air drying	dried pre-treated oven dried (105°C)
SR****)	14.0	13.5	23.5	22.5	20.5
Canadian Freenes	645	655	430	430	465
WRV 100 mesh**)	170	116	162	148	140
FiberLab****)					
- Length weighted	2.1 mm	2.2 mm	1.96 mm	1.92 mm	1.95 mm
- Fines length weighted	3.2 %	2.9 %	4.3 %	4.6 %	4.0 %
Zero span wet Nm/g*)	112	114	31	30	30

\*) ISO 15361:2000 (E) Pulps – Determination of zero-span tensile strength, wet or dry

\*\*\*) SCAN-C 62:00 WRV

\*\*\*\*) Fiberlab fiber analyzer – according to suppliers manual W4230467 V3.5 FI

\*\*\*\*\*) ISO 5267/1 Pulps – Determination of drainability – Part 1: Shopper-Riegler method

**Claims**

1. A method for the production of highly refined or microfibrillated cellulose, characterized in that the method comprises the steps of:
  - (a) treating cellulosic fibres to remove at least a major part of the primary  
5 wall of the fibres,
  - (b) drying the treated fibres,
  - (c) rewetting the treated fibres, and
  - (d) disintegrating the wetted fibres by mechanical means to obtain the final product.
- 10 2. The method of claim 1, characterized in that the fibres dried at step (b) are transported to be rewetted and disintegrated according to steps (c) and (d) at a different location.
3. The method of claim 1 or 2, characterized in that the fibres are dried to a water content of less than 20 wt-% at step (b).
- 15 4. The method of any one of the previous claims, characterized in that at step (a) primary wall material is removed by mechanical refining.
5. The method of any one of the previous claims, characterized in that at step (a) primary wall material is removed by oxidation, preferably by use of peroxide or ozone.
- 20 6. The method of any one of the previous claims, characterized in that at step (a) primary wall material is removed enzymatically, preferably by use of cellulase enzyme.
7. The method of any one of the previous claims, characterized in that primary wall material is removed by mechanical defibrillation combined with ox-  
25 idation and/or enzymatic treatment.
8. The method of any one of the previous claims, characterized in that microfibrillated cellulose (MFC) is produced at step (d) by use of a homogenizer and a fluidizer in succession.

9. Dried cellulosic pulp obtainable as an intermediate product of the method of any one of the preceding claims, characterized in that it has an average fibre length of at least 0.4 mm, while less than 50 % of the primary wall material of natural untreated fibres is left in the intermediate product.
- 5 10. The dried cellulosic pulp of claim 9, characterized in that the average fibre length is more than 70 %, preferably more than 80 %, more preferably more than 90 % of the average fibre length of the untreated fibres the pulp has been made from.
- 10 11. The dried cellulosic pulp of claim 9 or 10, characterized in that its content of fines with a fibre length less than 10  $\mu\text{m}$  is at most 5 wt-%.
12. The dried cellulosic pulp of any one of claims 9–11, characterized in that it has a water content of less than 20 wt-%.
13. The dried cellulosic pulp of any one of claims 9–12, characterized in that its Shoppler-Riegler (SR) drainage resistance is in the range of 20SR–50SR, 15 preferably 20SR–40SR, more preferably 20SR–35SR.
14. The dried cellulosic pulp of any one of claims 9–13, characterized in that its wet zero-span tensile strength is less than 60 Nm/g, preferably less than 50 Nm/g, more preferably less than 40 Nm/g.
- 15 20 15. The dried cellulosic pulp of any one of claims 9–14, characterized in that it has a BET surface of more than 40  $\text{m}^2/\text{g}$ , preferably more than 60  $\text{m}^2/\text{g}$ .
16. The dried cellulosic pulp of any one of claims 9–15, characterized in that it is in the form of stacked sheets, ready for transport to a different location.
17. A method for the production of the dried cellulosic pulp of any one of claims 9–16, characterized in that the method comprises the steps of:
- 25 (a) treating cellulosic fibres to remove at least a major part of the primary wall of the fibres, to obtain fibres with an average fibre length of at least 0.4 mm, and
- (b) drying the fibres obtained at step (a).
18. The method of claim 17, characterized in that the fibres are dried to a water 30 content of less than 20 wt-% at step (b).

19. The method of claim 17 or 18, characterized in that at step (a) primary wall material is removed by mechanical refining.

20. The method of any one of claims 17–19, characterized in that at step (a)  
5 ozone.

21. The method of any one of claims 17–20, characterized in that at step (a) primary wall material is removed enzymatically, preferably by use of cellulase enzyme.

22. The method of any one of claims 17–21, characterized in that primary  
10 wall material is removed by mechanical defibrillation combined with oxidation and/or enzymatic treatment.

23. Use of the dried cellulosic pulp of any one of claims 9–16 for the production of highly refined or microfibrillated cellulose.

## INTERNATIONAL SEARCH REPORT

International application No.  
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A. CLASSIFICATION OF SUBJECT MATTER		
IPC: see extra sheet		
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)		
IPC: C08L, D21B, D21C, D21H		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
SE, DK, FI, NO classes as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
EPO-Internal, PAJ, WPI data, COMPENDEX		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 20120135506 A1 (STORA ENSO OYJ ET AL), 13 January 2011 (2011-01-13); paragraphs [0035]-[0039]; claim 1 --	1-23
Y	US 4481077 A1 (HERRICK FRANKLIN W), 6 November 1984 (1984-11-06); column 3, line 23 - column 3, line 36; claim 1 --	1-23
X	SJOBERG, J "5.5 A new method for the determination of carbohydrates in surface layers of fibers (paper VI)" in: Characterization of chemical pulp fiber surfaces with an emphasis on the hemicelluloses: Royal Institute of Technology (KTH), Department of Fibre and Polymer Technology, Doctoral Thesis, 2002, Trita-PMT. 2002:12, pp. 40-41 --	9-15, 17, 21
<input checked="" type="checkbox"/>	Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> 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		"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
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"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
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	WO 2010116826 A1 (JUJO PAPER CO LTD ET AL), 14 October 2010 (2010-10-14); abstract --	1-23
A	WO 2012107642 A1 (UPM KYMMENE CORP ET AL), 16 August 2012 (2012-08-16); abstract -- -----	1-23

**Continuation of:** second sheet

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Information on patent family members

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