(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 September 2014 (25.09.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/147293 A1

(51) International Patent Classification:
D21C 3/02 (2006.01) *D21H 11/18* (2006.01)
D21C 9/00 (2006.01) *C08B 15/08* (2006.01)

(21) International Application Number:
PCT/FI2014/050190

(22) International Filing Date:
14 March 2014 (14.03.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20135281 22 March 2013 (22.03.2013) FI

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(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).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

[Continued on next page]

(54) Title: METHOD FOR PRODUCING NANO- AND MICROFIBRILLATED CELLULOSE

(57) Abstract: The field concerned is NFC or MFC production using chemical pulping. Herein is provided an environmentally friendly and improved pulping and papermaking method and dissolution and digestion method of cellulosic mate- rial. It is especially useful for treating chemical pulps. Consequently, improved products from these processes are provided. This improvement is achieved by changing the fiber structure in the pulping. Pulps may contain any type of cellulosic fibers, including wood and non-wood fibers.

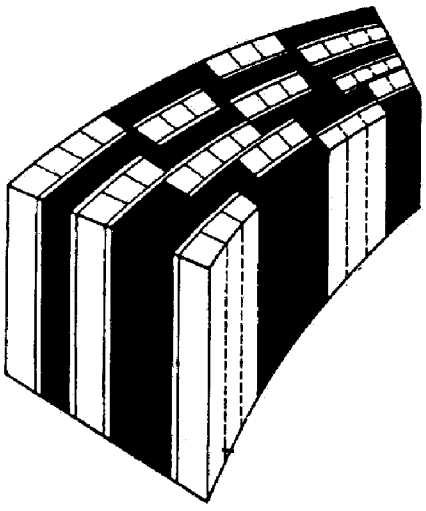


Fig. 3. B

WO 2014/147293 A1

Published:

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

Method for producing nano- and microfibrillated cellulose

FIELD OF THE INVENTION

The present invention relates to a method of producing nano- and microfibrillated cellulose. The present invention relates to a process of producing nano- and/or microfibrillated cellulose from cellulosic fibers yielding enhanced final product properties and higher productivity.

BACKGROUND OF THE INVENTION

Nanocellulose (NFC) or microfibrillated cellulose (MFC) is a material composed of nanosized cellulose fibrils with a high aspect ratio (length to width ratio). NFC production processes are generally based on treating chemical cellulose fibers. This can be done with enzymes or by changing swelling of the fiber by e.g. cationizing the fibers, acid hydrolysis, solvent treatments or ionic liquids. These pretreated fibers are next usually refined or fluidized in order to get the fibers deaggregated. These operations increase chemical and/or enzyme consumption and the energy consumption is very high. Significant amounts of water are also consumed and effluents are generated in these processes.

NFC production today commonly includes pulps from semichemical, mechanical and chemical pulping processes, which are used for pulping hardwood, softwood and non-wood raw materials. Various additives are used in order to improve economy in chemical consumption and washing of the pulp as well as the economy of the pulp production. Pretreatment of these fibers for NFC production includes various enzymatic, chemical and mechanical unit operations.

US-publication 2011/0277947 A1 presents a method for production of cellulose nanofilaments from bleached cellulose kraft pulps, e.g. hard and softwood pulps. These pulps are produced according to a prior art kraft process and the inventors claim that by using a special device, they may produce longer cellulose nanofilaments compared to the prior art.

US publication 2008/0057307 A1 teaches a method for production of nano-sized fiber fibrils from solid fibers having high aspect ratio. The raw materials useable in the embodiments can be selected from cellulose, acrylic and polyester fibers.

CA publication 2437616 A1 presents a method for production of cellulose nano filaments from cellulose kraft pulps. These pulps are produced according to prior art kraft processes and the inventors claim that by defibrating the pulp under higher shear forces they may produce NFC. US publication 5385640 presents a method for production of NFC (MDC) from wheat fiber and bleached sulfite cellulose pulps. The method comprises passing fibers through high shear in a double disc refiner.

In publication US 4869783 a chemical pulping process is disclosed wherein wood chips are partially defibrated such that the fibers in the chips are substantially separated from one another but sufficient inter-fiber bonding is maintained to preserve chip integrity and thereby to provide chips having an open porous fibrous network. To remove a majority of the lignin in the chips, they are then subjected to chemical pulping at an elevated temperature.

However, said publications do not recognize the need for internal fibril/aggregate separation in fiber cell wall during kraft cooking prior to washing, oxygen delignification and bleaching in order to increase product homogeneity and to decrease the energy consumption of the NFC production. There still is a need for NFC production methods of better yield and/or lower energy consumption.

SUMMARY OF THE INVENTION

It has been found in the present invention that when the fibers are chemically treated and the fiber cell wall in the chip matrix is at least partially deliginified, a pore structure is formed in the fiber cell wall which softens said cell wall. Therefore the cell wall can be mechanically modified without damaging the cell wall. In other words this can be described as increasing the void space between the cellulose aggregates as disclosed in application WO 2012/007642 and schematically illustrated in figure 3 B. It has been surprisingly found that fibers produced according to the invention can be cooked, oxygen delignified, bleached, washed and further treated by a pretreatment,

taking advantage of the increased accessibility of the cell wall, to produce nano- and microfibrillated cellulose.

In the pretreatment this fiber material is typically digested enzymatically, carboxymethylated or subjected to TEMPO-mediated oxidation and cationization in high consistency up to 50% solids. The pretreatment is followed by fibril removal from the pulp fibers, for example, with a Masuko-collider or fluidizer to yield NFC or MFC. The present invention is not limited to these pretreatments or further treatments, but also other methods can be used for production of NFC or MFC.

Use of high pulp consistency decreases the water consumption in the pulp production and investment costs significantly. By this procedure, significant energy saving can be obtained, optionally together or as an alternative to increased NFC viscosity.

An objective of the present invention is thus to provide environmentally friendly and improved pulping and papermaking methods and dissolution and digestion methods for cellulosic material in NFC or MFC production. The present invention is especially aimed at producing chemical pulps to be used for NFC production. According to the present invention this improvement is achieved by changing the fiber structure in the pulping.

Pulps may contain any type of cellulosic fibers, including wood and non-wood fibers, originated from virgin wood, or non-wood fiber sources or combinations thereof.

Contrary to results obtained in the prior art, it was also unexpectedly found that the yield of the kraft cooking process remained the same and no increase in wood consumption was observed. By applying the method of the invention, the amount of water required for washing the pulp and the energy consumption in the NFC production by grinding or fluidizing all decreased. Accordingly, employing the invention also yielded decreased chemical consumption.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates the damage on the fiber wall caused by the prior art methods, which methods aim at the removal of fibers from the chip matrix to be continued with cooking or bleaching processes. In this way the cell wall will remain intact or will be partially removed/damaged. Typical damages to the cell wall in wood chip fiberizing are indicated for different pulping processes. In this picture, (RMP refers to Refiner Mechanical Pulping, TMP refers to Thermo Mechanical Pulping, CTMP refers to Chemo-thermo-mechanical Pulping, P refers to primary cell wall, S_1 refers to Secondary cell wall 1, S_2 refers to Secondary cell wall 2, S_3 refers to Secondary cell wall 3, ML refers to middle lamella).

Figure 2 represents schematically an example of a continuous kraft cooking system. Positions marked with numbers 1, 2, 3 and 4 show sites, wherein the treatment according to embodiments of the present invention can be applied during or after impregnation. Positions 5, 6, 7, and 8 show other embodiments where the modified pressing and shearing devices can be placed in the cooking stage in the digester and after the digester of the continuous cooking system. Figure 3 A explains schematically the structure of a cross-cut cellulose fiber.

Figure 3 B explains as a before (left) and after (right) presentation the generation of pores and softening of the fiber cell wall in the cooking according to the present invention, wherein the letters P, S_1, S_2 and S_3 have the same meaning as in figure 1. In figure 3 B, the black areas denote lignin or lignin-hemicellulose and white blocks cellulose aggregates or protofibrils.

Figure 3 C illustrates a wood chip cross-cut and points out the direction in which the mechanical treatment according to the present invention, such as shearing, affects the fiber cell wall.

Figure 4 describes the transformation caused by the treatment according to the present invention as AFM (atomic force microscopy) and SEM (scanning electron microscopy) pictures. Figure 4 A is AFM picture taken after pretreatment which has opened the fiber cell wall pore structure. Pretreatment provides increased accessibil-

ity of the cell wall and more efficient enzymatic efficiency. Figure 4 B has been taken with SEM after further processing into NFC with e.g. a Masuko collider or fluidizer. This step exhibits lower energy consumption because of the opened cell wall structure (and improved enzymatic digestibility).

DETAILED DESCRIPTION OF THE INVENTION

The main challenge in NFC production is high energy consumption in separating cellulose aggregates from cellulosic fibers.

For this purpose, here is disclosed and claimed a method of producing NFC or MFC from a cellulosic fiber source. As simplest, this method may be described to comprise chemical pulping wherein physical/mechanical treatment selected from pressing and shearing is applied to impregnated pulp, followed typically by cooking, washing and bleaching, and a further refining with enzymes or solvent and finally the NFC grinding. Experimentally, this has now been shown to decrease the energy consumption in NFC production. Further, better NFC yield has also been proven by said experiments for NFC obtained by the method of the present invention.

More specifically, the present method may be described and claimed as a method of producing NFC or MFC from a cellulosic fiber source, comprising at least steps a), d) and e) in the order given below

a) chemical pulping, wherein a physical/mechanical treatment step selected from pressing or shearing impregnated cellulosic fiber source, is applied during or after impregnation or during or after cooking in the pulping process, wherein a change in the fiber wall cell structure is effected and the conditions in said treatment comprise
    i. an alkali charge of 10 % - 40% effective alkali as NaOH on cellulosic fiber source, such as on wood,
    ii. a temperature effective for increasing the swelling of the hemicelluloses and/or the lignins and for reaching a material softening point,
    iii. a pulp consistency of 1- 50 %,

iv. a kappa number between 150 and 5,

b) an optional washing step,

c) an optional bleaching step,

d) a pretreatment step, which takes advantage of the increased accessibility of the fiber source, and

e) a removal of the fibrils of the fiber cell wall.

It is essential that the fiber material to be pulped, e.g. wood chips, is impregnated prior to applying the treatment according to the present invention which is then followed by processing into NFC. Preferably said impregnation is conducted under pressure. It can be applied to chemical pulping, wherein the preferable application is the kraft pulping process. The stages in the continuous kraft cooking processes are impregnation, transfer circulation and cooking. In the batch cooking processes the treatment of the present invention can be performed in the same process stages as in the continuous process. It has been in the present invention unexpectedly found that some or all the benefits discussed above can be achieved by applying physical/mechanical treatment to raw material in the process of chemical pulping. More specifically, herein is provided a method of processing chemical pulp to be refined into NFC, in which process a change in the fiber wall is affected by treating impregnated cellulosic fiber source physically.

Raw materials applicable in this method may contain any type of cellulosic fibers, including wood and non-wood fibers or possibly mixtures thereof. Cellulosic refers to fibers comprising cellulose, preferably as the main component. A preferable cellulosic fiber source comprises wood chips. Said cellulosic fibers may be treated by alkaline conditions, or bleached by any bleaching method. However, preferably fibers are bleached after treatment according to the invention. Non-wood material here refers to cellulosic fibers other than wood which are applicable to pulping, and known to a person skilled in the art.

As used herein, “treatment” or “treatment according to the invention” refers to applying to a chemical pulping process the step of physical/mechanical treatment conventionally absent from such processes. The method of the invention comprises said

treatment. Here, by "physical/mechanical treatment" is meant any means of importing to the chemical pulping physical energy to affect the chips and/or fibers. Preferably the physical/mechanical treatment of the present invention is performed by inducing pressure forces, pressing or shearing to the fibers at the above-mentioned conditions so that the fiber wall structure changes. It is advantageous to treat the cellulosic material, e.g. the wood chips, into cross direction of the fibers in the wood chips. Preferably the pressing or shearing of the wood chips is applied in the cross direction of the wood chips and so that the volume of the chips decreases e.g. to half of the original volume. It is also not necessary that the fibers are removed from the wood chip.

In the method of the present invention, said physical/mechanical treatment is preferably selected from pressing or shearing said fiber source, i.e. impregnated cellulosic fibrous material. A person skilled in the art could find other means for introducing physical energy into the system, but pressing or shearing are readily applicable to existing equipment.

The energy applied to the system during the physical/mechanical treatment step ranges preferably from 1 to 100 kWh/t. Applying energy in the form of physical/mechanical treatment during transfer circulation or cooking stages or therebetween is contrary to the teaching of common energy economics of kraft pulping. However, it has now been found that the overall benefit for the process in its entirety exceeds the value gainable by energy trade.

Other conditions for said treatment comprise alkali charge of 10 - 40 %, preferably a high alkali charge, preferably 15-35 % effective alkali as NaOH on cellulosic fiber source, such as wood chips. Said conditions further comprise an effective temperature for increasing the swelling of the hemicelluloses and/or the lignin to reach their material softening point. When selecting the temperature, said treatment temperature is preferably from 50 to 200 ˚C. When the treatment according to invention is effected in at least one position selected from positions (3-8) as shown in figure 2, said treatment temperature is preferably from 120 to 185 ˚C. The change in the fiber structure is preferably performed in the conditions of high alkali charge and temperature so that the hemicelluloses and the lignin have reached their material softening points

(Gorig 1961 and Salmen 1982). The wood chips could be also preferably partially delignified so that the middle lamella holds the chips together and the kappa number of the chips is for example between 110 and 5.

Generally, the method of the invention may be applied in at least one stage in the kraft pulping process selected from transfer circulation and cooking. The treatment can thus be incorporated into normal process steps involved in kraft pulping.

The invention is discussed in more detail in the following examples with reference to the appended drawings, Figure 2 shows typical digester arrangements, in which the physical/mechanical treatment of the cellulosic fibers, such as wood chips, can be carried out during or after impregnation. The treatment herein means pressing and/or shearing the impregnated wood chips at elevated temperatures so that the fiber matrix in the chip will be broken. The shearing and pressing can be performed with e.g. a conical plug feeder (US Patent 5570850) modified so that the surfaces of the feeder will provide this action (e.g. according to US Patent 4953795) in one or several of the positions numbered as 1, 2, and 4 in Fig. 2a. The positions are as follows: 1. Top of the impregnation vessel; 2. Bottom of the impregnation vessel; 3. Transfer circulation; and 4. Top of the digester vessel. 5. and 6. Inside the digester vessel. 7. Bottom of the digester vessel; and 8. Pulp line after the digester. The shearing and pressing at the position 2 and 7 can be carried out with a modified bottom scraper (US Patent 5736005), which provides the action mentioned above by providing it with shearing plates. Other devices which can be applied after modification to these positions 1 to 4 are feed screws, pumps or presses according to, for example, US Patents 4915830 or 6036818, US Patent 5622598 or US application 20050053496 and US Patent 4121967.

The shearing and pressing can be performed with a conical plug feeder (US Patent 5570850) modified so that the surfaces of the feeder provide this action (e.g. according to US Patent 4953795) in the positions 3 and 8 in the Fig. 2. This does not mean that other devices providing the similar action could not be used. The shearing and pressing at the positions 5, 6 and 7 can be carried out with a modified bottom scraper (US Patent 5736005), which provides the action mentioned above e.g. by providing

it with shearing plates. Also these positions can be provided with any kind of mixer or screw or press providing a shearing and pressing action on the fiber matrix. The position 8 can be provided with feed screws, pumps or presses after modification. Feasible examples can be found in US patents 4915830 or 6036818, US patents 5622598 and 4121967 or in US patent application 20050053496. All of these modifications can be performed by a person skilled in the art.

Any one of the above-mentioned positions alone or any combination of these positions can be used in the method of the present invention. The combination of these positions is dependent on the properties of the pulp which are desired after cooking. The conditions can be typical to the kraft cooking process in the current positions or they can be modified to desired positions. The surprising dewatering properties, which decrease the flow resistance characteristics are best observed and benefited when the method of the invention further comprises washing in the digester and subsequent washing stages, oxygen delignification and/or bleaching. After these steps it was also surprisingly found that when these fibers were digested enzymatically, or carboxymethylated, or subjected to TEMPO-mediated oxidation and cationization followed by fibril removal from the pulp fibers with a Masuko collider or fluidizer, significant energy savings were obtained, together with increased NFC viscosity. In other words, porous pretreated cellulose fibers are fibrillated in a Masuko mass collider or fluidizer in order to separate fibrils from the porous fiber cell wall, whereby NFC or MFC is obtained.

It should be understood generally that internal fibril/aggregate separation in the fiber cell wall during kraft cooking as used herein, means a change in the fiber referring to modification of the individual or agglomerated fibers, which affects at least part of the fiber wall, separating it to its constituents. One preferable example is increasing the porosity of the fibers, in other words, affecting a change in the fiber cell wall structure by increasing the size of the pores in the fiber cell wall. Porosity refers to cell wall porosity as measured with atomic force microscopy (AFM). Internal fibril/aggregate separation in the fiber cell wall can be seen as an increase in the pore size distribution measured with atomic force microscopy (AFM, Fahlen 2005) from resin bedded

cross sections of the fiber cell wall while the chemical composition or kappa number remains unchanged.

The flow resistance can be determined by pressing a column of fibers with a force and monitoring the increase in the flow pressure over the column. It was surprisingly found that the pressure increase decreased when fibers were manufactured according to the invention. This allows one skilled in the art to run the process in higher pulp consistency than the medium pulp consistency 15% normally practiced in the art. Hence, according to the present invention, the medium pulp consistency in the physical/mechanical treatment step of the present method may be up to 50 %, preferably up to 40%, or more preferably between 5 % and 40 %.

The following stage can be one of the following or any combination thereof: washing, oxygen delignification, bleaching, enzymatic digestion, carboxymethylation, subjecting to TEMPO-mediated oxidation, cationization and drying. However, independent of the number of the stages after pulp production according to the invention the final two stages need to be enzymatic digestion or carboxymethylated or subjected to TEMPO-mediated oxidation and cationization mechanical fibrillation with a fluidizer or refiner know in the art. The drying can be performed between these two stages or it can be omitted.

The present process comprises a pretreatment step, which takes advantage of the increased accessibility of the fiber source, for production of NFC or MFC. Pretreatments known to a person skilled in the art comprise subjecting an opened cell wall to enzymatic digestion, ionic liquid modification or carboxymethylation or TEMPO-mediated oxidation or cationization. Preferably the pretreatment is selected from enzymatic digestion and solvent pretreatment. It was also surprisingly found that enzymatic treatment efficiency increased when fibers were produced according to the invention, which was seen as a higher viscosity drop of the fibers after the treatment, indicating higher accessibility of the cell wall of the fibers.

The conceptual process steps comprise the following:

In kraft cooking conditions: Effective alkali (EA) 20% and temperature 165 °C, lignin in the fiber cell wall (A) and the cell wall is softened and a porous (B) fiber cell wall is created, which here is defined as the process of Fig. 3 (C). The internal fibril/aggregate separation in the fiber cell wall during kraft cooking according to the invention (D):

This softened and porous fiber cell wall is pressed in the cross direction (as disclosed in Figure 3 C) of the longitudinal axis of the fibers axis in the wood chips under the conditions of the invention and internal fibril/aggregate separation in the fiber cell wall during kraft cooking as used herein will occur, a change in the fiber refers to modification of the individual or agglomerated fibers, which affects at least part of the fiber wall, separating it to its constituents. In Fig 4 is presented separation of the (A-B) nanofibrils according to invention. The opened cell wall (A) is subjected to enzymatic digestion, or carboxymethylation or TEMPO-mediated oxidation and cationization and then pulp is fibrillated with a Masuko collider or fluidizer.

EXPERIMENTAL PART

The effects obtainable by embodiments of the method according to the invention are proven by the following experiments, which should not be considered as limiting the scope of the invention. With the abbreviation REF is referred to conventional methods, i.e. samples treated according to prior art procedures.

Example 1

In this example eucalyptus wood pulp was produced both according to the invention and as reference (REF), conventionally with cooking at 165 °C with 20% alkali charge. The results are shown in table 1. The wood chips were pressed and sheared cross-directionally to the fiber direction. The energy applied was 11 kWh/t.

Table 1.

Analysis	REF eucalyptus pulp	Method applied in position 5 of figure 2 for eucalyptus pulp
Kappa number	19	18
Cooking yield,%	54	54
Viscosity, ml/g	850	840

The pulp column flow resistance was measured with the following experiment, which measures the liquid pressure difference over the digester column. The amount of pulp which was used was 500g. The fiber column resistance was measured so that the column was pressed with 2 bar pressure and water flow was pressed through the pad with increasing pressure from 1 to 7 bar.

The liquor flow resistance results are presented in Fig. 5. In the Y-axis is shown liquor flow ml/s and in the x-axis is shown consistency (%). Fig 5. shows that it is practically impossible to use a reactor with pulp consistencies higher than 20% with REF, while the pulp consistency can be increased up to 40% according to the invention (EPD). This allows very low water consumption in the process stages.

In table 2 are presented the bleaching and enzymatic digestion conditions. 500g of each pulp was prepared under the conditions presented in the table. Also the viscosities before and after the enzymatic digestion are presented.

Table 2. Bleaching and enzymatic digestion conditions. D: ClO2 stage, E: alkali extraction, X:entzymatic digestion. REF: reference and EPD: sample prepared according to the invention.

		REF	EPD
D0-stage	ClO_2 charge, % act.Cl	3,62	3,80
Consist. 9%	ClO_2 consumed, % act.Cl	3,62	3,80
60 °C, 60min	*H_2SO_4 charge, %	0,48	0,49
	final pH (slurry at °C)	2,2	2,1
E1-stage	NaOH charge, %	1,45	1,52
Consist. 10%	final pH (slurry at °C)	11,0	11,1
70°C, 60min	Brightness, %	69,3	72,7
	Kappa number	4,81	4,48
D1-stage	ClO_2 charge, % act.Cl	1,30	1,21
Consist. 9%	ClO_2 consumed, % act.Cl	1,30	1,21
70 °C, 120min	*NaOH charge, %	0,10	0,10
	final pH (slurry at °C)	3,8	3,9
	Brightness, %	85,1	86,8
D2-stage	ClO_2 charge, % act.Cl	0,50	0,40
Consist. 9%	ClO_2 consumed, % act.Cl	0,42	0,27
70°C, 180min	*H_2SO_4 charge, %	-	-
*for pH adjustment	final pH (slurry at °C)	5,1	5,4
	Brightness, %	91,1	91,4
	Kappa number	0,96	0,98
	Bleaching yield, %	96,1	95,5
	Viscosity, ml/g	1290	1160
	Dry matter content, %	28,02	30,61
	Tot. ClO_2 cons.% act.Cl	5,34	5,28
		3293	**3292**
		REF+X	**EPD+X**
X-stage	Initial pH	4,8	4,7
Ecopulp R 100 ml/t	Final pH	4,9	4,8
Consist. 10%	Viscosity, ml/g	1140	970
60°C	Dry matter content, %	27,85	29,83
75 min			

From table 2 it can be concluded that with pulp according to the invention a 26% (150 vs. 190 ml/g) viscosity decrease is achieved with the same chemical charge.

The pulps at the amount of 100g each were then fibrillated at target concentration during fibrillation of 2%. The fibrillation equipment was a Masuko Super mass collider MKZA10-15J.

Pulp produced according to the invention was treated with enzymes in the same manner as the pulp produced according to conventional methods. These four pulps were grinded with a Mazuko mass collider at 3 different levels of the energy applied to the fibers as kWh/kg of pulp. The NFC amount is presented as particles of sizes between 1-100 nm and MFC particles between 100-1000 nm (included in the same

value as %), the viscosity defines the homogeneity of the nano- or micro-sized material; the higher the more homogenous. The refining results are presented in Table 3.

Table 3.

Analysis	REF eucalyptus pulp	Eucalyptus pulp produced according to invention	REF with enzyme treatment	pulp produced according to invention with enzyme treatment
Energy	23 kWh/kg	3 kWh/kg	3.5 kWh/kg	2 kWh/kg
Amount of NFC, (%) of the pulp	10%	15%	15%	25%
Viscosity at 8kWh/t, mPa	35000	45000	35000	50000

The above results confirm that surprisingly the pulp produced according to the method of the present invention has much lower energy consumption in NFC production in comparison to pulp which is produced in a conventional way. Also the amount of NFC produced is higher when pulp is produced according to the method of the present invention compared to conventional methods.

References:

1. Goring, D.A.I.,The physical chemistry of lignin. Proceedings of the Wood Chemistry Symposium (I.U.P.A.C.),. Montreal, Canada, 1961. Pp. 231- 254.
2. Salmen, L., Temperature and water induced softening behavior of wood fiber based materials. Department of Paper Technology, The Royal Institute of Technology. Stockholm, Dissertation 1982, 114p.
3. Fahlen, J. The cell wall ultrastructure of wood fiber effects of chemical pulp fiber line, KTH 2005, 55p.

Claims:

1. A method for producing nano- (NFC) or microfibrillated cellulose (MFC) from a cellulosic fiber source, comprising at least steps a), d) and e) in the order given below

   a) chemical pulping of the cellulosic fiber source, wherein a physical/mechanical treatment step selected from pressing or shearing of impregnated cellulosic fiber source is applied during or after impregnation or during or after cooking in the pulping process, wherein the conditions in said treatment comprise

      i. an alkali charge of 10 % - 40% effective alkali as NaOH on cellulosic fiber source,
      ii. a temperature effective for increasing the swelling of the hemicelluloses and/or the lignins and to reach a material softening point,
      iii. a pulp consistency of 1-50 %, and
      iv. a kappa number between 150 and 5,

   b) an optional washing step,
   c) an optional bleaching step,
   d) a pretreatment step, which takes advantage of the increased accessibility of the fiber source, and
   e) removal of the fibrils of the fiber cell wall to produce NFC or MFC.

2. The method according to claim 1, wherein said cellulosic fiber source comprises wood chips.
3. The method according to claim 1 or 2, wherein the chemical pulping comprises kraft pulping.
4. The method according to claim 2, wherein the wood chips are treated into cross direction of the fibers in the wood chip.
5. The method according to any one of the previous claims, wherein the wood chip volume decreases in said physical/mechanical treatment.

6. The method according to any one of the previous claims, wherein the conditions in said treatment comprise an alkali charge of 15-35 % effective alkali.
7. The method according to any one of the previous claims, wherein said treatment temperature ranges from 50 to 200 °C, and preferably from 120 to 185 °C.
8. The method according to any one of the previous claims, wherein the structure of the fiber cell wall is changed in step a) and said change in the fiber cell wall structure comprises increasing the size of the pores in the fiber cell wall.
9. The method according to any one of the previous claims, wherein said physical/mechanical treatment affects an increase of the porosity of the fibers as measured with AFM.
10. The method according to claim 2, wherein said physical/mechanical treatment comprises applying force into wood chips in cross-directional direction in relation to said chips.
11. The method according to any one of the previous claims, wherein said physical/mechanical treatment comprises applying energy from 1 to 100 kWh/t.
12. The method according to any one of the previous claims, wherein said treatment is applied in at least one further stage in the kraft pulping process selected from impregnation, transfer circulation and cooking.
13. The method according to any one of the previous claims, wherein said treatment is applied in at least another process step selected from before the kraft pulping process, in the kraft pulping process or after the kraft pulping process.
14. Nanocellulose (NFC) produced by the method according to any one of claims 1-13.
15. Microfibrillated cellulose (MFC) produced by the method according to any one of claims 1-13.

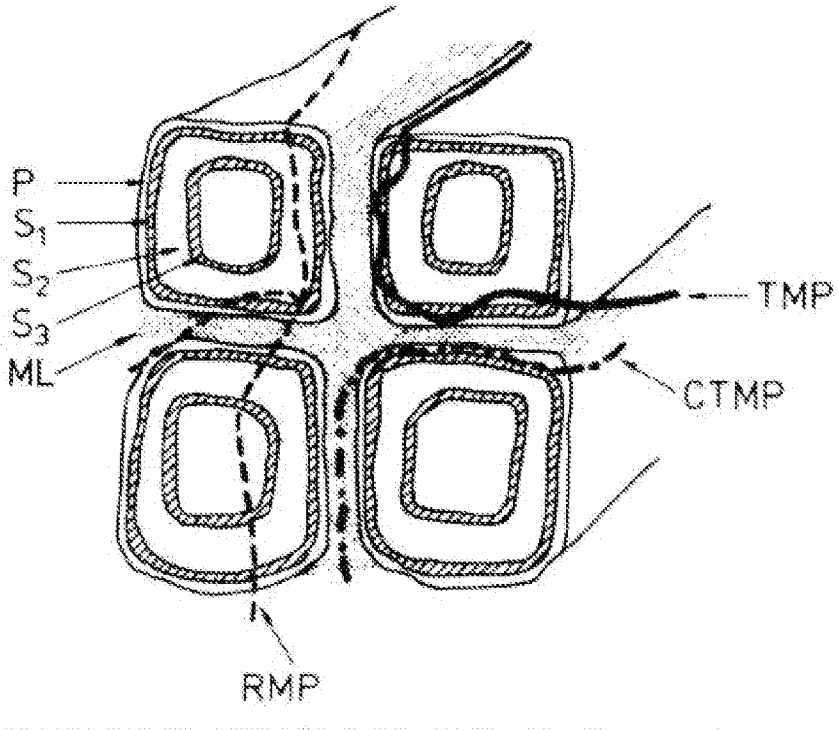


Fig. 1.

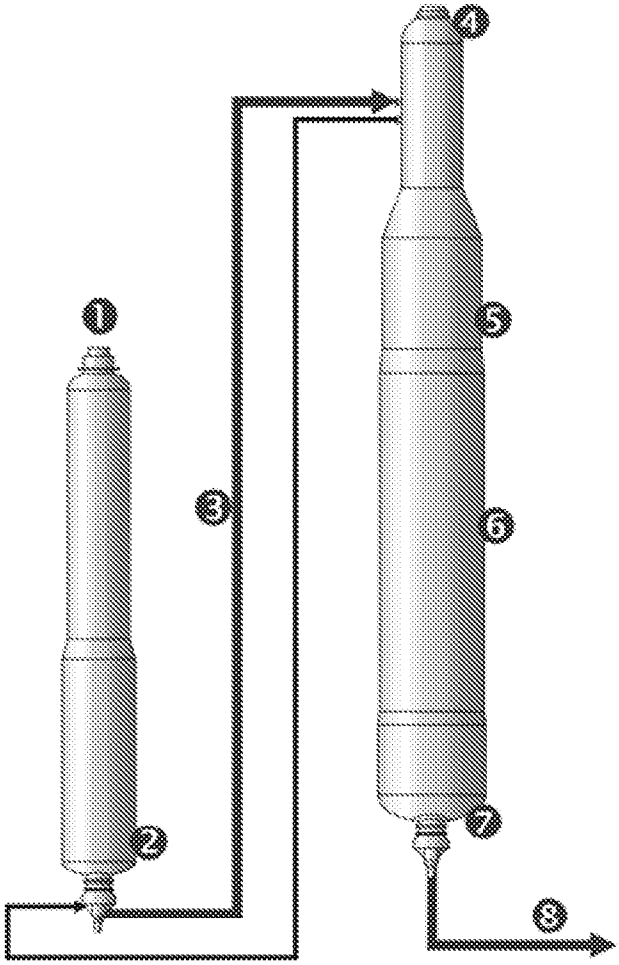
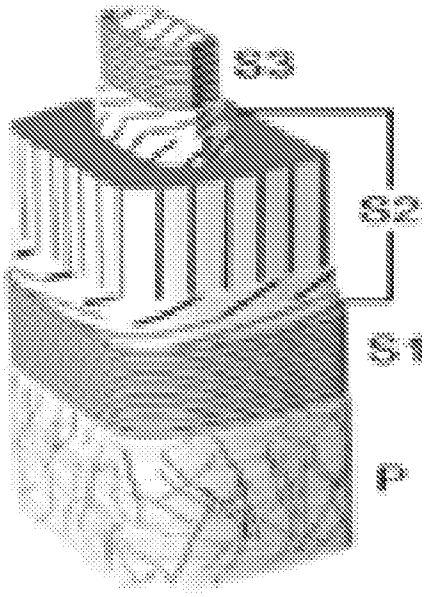


Fig. 2



3 A

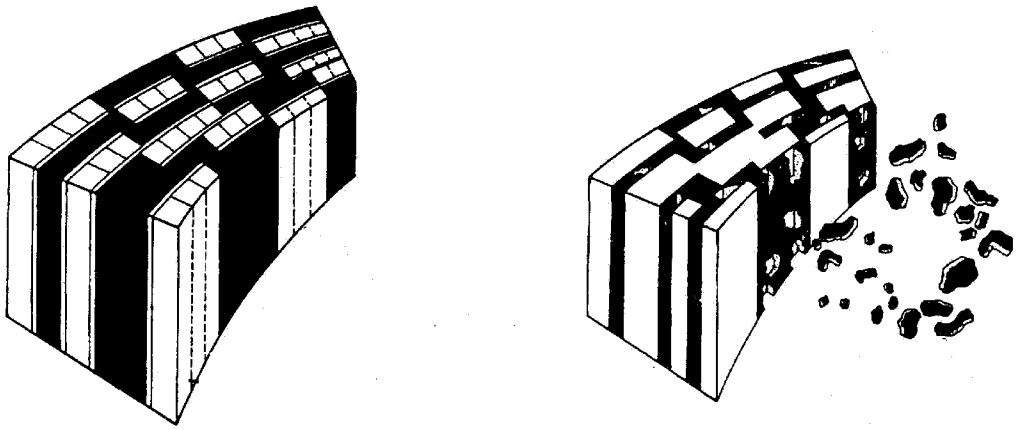


Fig. 3. B

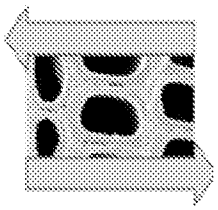
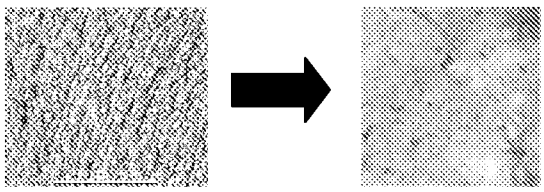


Fig 3 C.



A B

Fig. 4.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2014/050190

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21C3/02 D21C9/00 D21H11/18 C08B15/08
ADD.

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 D21H C08B

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 practicable, 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.
X	JP 2012 219413 A (OJI PAPER CO) 12 November 2012 (2012-11-12)	1-15
Y	abstract paragraph [0019] - paragraph [0024] paragraph [0041] - paragraph [0049] -----	1-15
Y	WO 2012/007642 A1 (JOUTSIMO OLLI [FI]) 19 January 2012 (2012-01-19) cited in the application claims 1-11 examples 1-13 page 8, line 1 - page 11, line 22 -----	1-15
Y	US 2011/277947 A1 (HUA XUJUN [CA] ET AL) 17 November 2011 (2011-11-17) cited in the application the whole document -----	1-15

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

☒ See patent family annex.

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"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 June 2014	07/07/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Naeslund, Per

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/FI2014/050190

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2012219413 A	12-11-2012	NONE	
WO 2012007642 A1	19-01-2012	EP 2593248 A1	22-05-2013
		US 2013105097 A1	02-05-2013
		WO 2012007642 A1	19-01-2012
US 2011277947 A1	17-11-2011	CA 2799123 A1	17-11-2011
		CN 103038402 A	10-04-2013
		EP 2569468 A1	20-03-2013
		JP 2013526657 A	24-06-2013
		US 2011277947 A1	17-11-2011
		WO 2011140643 A1	17-11-2011