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(54) PROCESS FOR THE PRODUCTION OF MICROFIBRILLATED CELLULOSE FROM HIGH-YIELD KRAFT PULP, MICROFIBRILLATED CELLULOSE OBTAINABLE BY SAID PROCESS AND KRAFT PULP AND PAPER PRODUCTS COMPRISING SAID MICROFIBRILLATED CELLULOSE

(57) The present invention relates to a process for the production of microfibrillated cellulose from a high-yield pulp, comprising the steps of selecting a Kraft pulp with a total lignin content of 5% to 30° by weight and its defibration until obtaining a suspension of microfibrillated cellulose with a minimum fine content of 15° by weight.

Other aspects of the present invention correspond to the microfibrillated cellulose obtainable by the process and the Kraft pulp and paper products comprising the microfibrillated cellulose. The process described allows the production of microfibrillated cellulose with lower energy consumption and the microfibrillated cellulose has increased papermaking ability, resulting in paper products with increased mechanical strength properties.

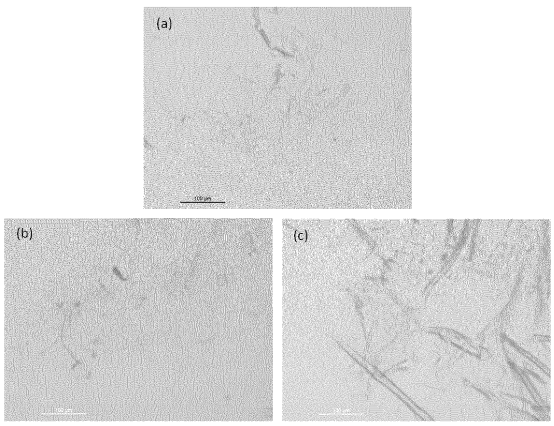

Figure 1

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Description

TECHNICAL FIELD

[0001] The present invention relates to a process for the production of microfibrillated cellulose from high-yield Kraft pulp. Furthermore, the invention concerns the microfibrillated cellulose obtainable by the process, and the Kraft pulp and paper products comprising the obtained microfibrillated cellulose. The invention has application in the field of the paper industry.

BACKGROUND ART

[0002] Microfibrillated celluloses have been the target of increasing interest for different applications, namely in the area of pulp and paper production. They can be produced from different raw materials such as, for example, cellulosic fibers from, wood, lignocellulosic plants, herbs and tubers, among others, and through processes that may involve enzymatic, chemical and mechanical operations, individually or in several stages (Klem et al, Nanocelluloses: A New Family of Nature-Based Materials, Angew. Chem., Int. Ed., 2011, 50, 5438 - 5466).

[0003] Conventionally, microfibrillated celluloses are produced from pulp that has been delignified and preferably bleached (Osong et al., Processing of wood-based microfibrillated cellulose and nanofibrillated cellulose, and applications relating to papermaking: A review, 2016, 23, 93-123; Klemm et al., Nanocellulose as a natural source for groundbreaking applications in materials science: Today's state, Materials Today, 2018, 7, 720-748).

[0004] In fact, and as shown in the documents mentioned below, microfibrillated cellulose production processes are carried out from conventional cellulosic raw materials, that is, cellulosic pulps delignified by typical chemical cooking processes, such as Kraft or sulfite, and/or bleached, thus typically having total lignin contents inferior to 5% by weight. Likewise, the documents that report the use of microfibrillated cellulose in the production of paper material consider it in accordance with its conventional definition regarding the raw material, and its properties, which originate it.

[0005] Patent EP3341523B1 discloses a method of producing microfibrillated cellulose that requires fewer passes through refiners and, consequently, lower energy consumption, which involves refining, with blades of certain dimensions, of a chemical pulp of cellulosic fibers.

[0006] Patent EP2494107B1 concerns a process for producing microfibrillated cellulose with the aid of an extruder, in which at least one chemical product (among carboxymethylcellulose, methylcellulose, polyvinyl alcohol, calcium stearate, alcohols, surfactants and tensioactives or other hydrophobic chemical products) is added to the extruder during processing of a mixture of fibers, preferably cellulosic but cotton fibers and fibers from agricultural products such as potatoes and cereals can also be included.

[0007] Patent application EP2196579A1 describes a method of producing microfibrillated cellulose, with a lower associated energy consumption, which involves passing a suspension of a cellulose pulp in a solvent (such as water, alcohols, dimethylsulfoxide, glycerol and mixtures thereof) through a hole of a homogenizer so that said suspension is subjected to a pressure drop. Said diameter of said hole is from 100 to 700 μm and said pressure drop has a maximum value of 100 MPa. The cellulose pulps described in the patent application refer to conventional pulps and those obtained by typical production processes, such as bleached, semi-bleached and unbleached pulps, by sulfite and sulfate chemical processes.

[0008] The patent application WO2014147293A1 discloses a microfibrillated cellulose production process which incorporates, in the chemical cooking, a physical/mechanical treatment, such as pressing and shearing, of an impregnated cellulosic fiber source, a treatment that is applied during or after the impregnation of the fiber or during or after fiber cooking, in which a change in the cellular structure of the fiber wall is observed, thus decreasing the energy consumption involved in the production of the microfibrillated pulp. The process then continues with the typical cooking steps, for example by Kraft cooking, washing and bleaching, and further refining with enzymes or solvent and, finally, the milling of the obtained fibril. The invention describes the use of fibers from herbaceous and non-herbaceous and combinations thereof.

[0009] The patent EP2576629B1 describes a method of producing microfibrillated cellulose, said to be more efficient and cost-effective compared to the prior art, which involves acid hydrolysis at elevated temperature or acidification followed by washing and hydrolysis at elevated temperature of a cellulosic material. The lignin content of the cellulosic starting material is inferior to 5% by weight. As a cellulosic material, it is considered chemical pulp of hardwoods or softwoods, bleached or unbleached, such as Kraft, sulfite and soda pulp.

[0010] Patent EP2452014B1 describes a microfibrillated cellulose production process, more efficient compared to the prior art, which consists of processing a pulp of cellulosic fibers with an enzyme and a mechanical treatment, in which both are carried out simultaneously in a single step. Bleached fibers are used, for example softwood and hardwood fibers, since, as described in the aforementioned patent, the presence of lignin in unbleached pulps leads to greater energy consumption in the production of microfibrillated cellulose.

[0011] Patent application US20160273165A1 discloses a method for producing a paper product with improved strength and filler and fine retention, which involves adding an anionically modified microfibrillated cellulose to a fiber suspension in an amount of 0,1 to 10% by weight.

[0012] Patent application EP3433428A4 describes a paperboard with improved compression strength involving the use of a cellulose pulp with drainability values between 15 and 28 (in Schopper-Riegler values) to which it is added between 1 and 5% by weight of microfibrillated cellulose and a hydrophobic additive such as an alkylketene dimer, succinic anhydrides, rosins and a styrene maleic anhydride, or emulsions, modifications and mixtures thereof.

[0013] EP2978894B1 describes a process for producing paper and paperboard with strength properties through a mixture of fibers which involves the addition, in a specific sequence, of microfibrillated cellulose, strength additives and microparticles such as silica and bentonite, to this mixture of fibers.

[0014] One of the most industrially used chemical processes for the production of pulp from wood is Kraft cooking, or sulfate cooking. This chemical process consists of cooking the wood in a cooking liquor usually consisting of sodium hydroxide and sodium sulfide, at temperatures of around 140 to 180 °C, in pressurized reactors (Ek, Monica; Gellerstedt, Göran; Henriksson, Gunnar; Pulp and Paper Chemistry and Technology Volume 2, Pulping Chemistry and Technology, 2009, De Gruyter, Berlim). This chemical cooking process typically ends with a total lignin content inferior to 5% by weight. It is necessary to extend the Kraft cooking process to lignin contents inferior to 5°, in order to be able to process the pulp, either for direct paper production or for subsequent bleaching. The Kraft cooking process is one of the processes typically used to produce the raw material used in state of the art microfibrillated cellulose production processes.

[0015] The low lignin content in the cellulose pulps used as starting pulps for the production of cellulose fibrils, obtained by delignification of wood by chemical processes and by additional bleaching steps, is necessary and, as such, a conditioning factor for the application of production methods of these cellulose fibrils that require lower mechanical and chemical energy costs, as demonstrated by Chaker and co-authors who, when evaluating the suitability of cellulose pulps for fibrillation, chose an initial pulp with a lignin content inferior to 20% by weight and to which they apply an additional bleaching step after cooking, in order to additionally reduce the lignin content to values substantially inferior to 5%, typically inferior to 1%, so as to reduce the influence of the presence of lignin in the fibrillation of the cellulose pulp (Chaker et al., Key role of the hemicellulose content and the cell morphology on the nanofibrillation effectiveness of cellulose pulps, Cellulose, 2013, 20, 2863 - 2875).

[0016] Thus, the state of the art shows that the methods to produce microfibrillated cellulose, from the cellulosic materials conventionally used for microfibrillated cellulose production, understood as cellulosic pulps delignified by the typical chemical cooking processes, as Kraft or sulfite, and/or additionally bleached, include modifications, for increased efficiency and lower associated costs, involving the use of, for example, organic solvents, chemical treatments, such as hydrolysis, and fibrillation equipment developed for this purpose, in several stages or in combination. Cellulose pulps with a lignin content substantially inferior to 5% are also used as raw material, applying, for that, for example, bleaching treatments to the original cellulose pulps.

[0017] There is thus a need for a microfibrillated cellulose production process which exempts the raw material from the application of complex chemical and/or mechanical treatments aiming at reducing the lignin content of the referred raw material to values inferior to 5% in weight and which also dismiss such treatments during its conversion into microfibrillated cellulose. There is also a need for a microfibrillated pulp production process that provides lower energy consumption, thus lower associated costs, and results in the production of a microfibrillated pulp that can be applied in the production of paper materials with increased strength properties, compared to microfibrillated celluloses produced by state of the art production processes using conventional cellulosic raw materials, i.e. with lignin contents inferior to 5%.

SUMMARY OF INVENTION

[0018] In a first aspect of the present invention it relates to a process for the production of microfillated cellulose wherein the process comprises the steps of:

a) selecting a Kraft pulp with a total lignin content of 5 % to 30 % by weight;
b) mechanically defibrating the pulp selected in step a) until obtaining a microfibrillated cellulose suspension with a minimum fines content of 15% by weight.

[0019] A second aspect of the present invention relates to a microfibrillated cellulose obtainable by the process according to the first aspect of the invention.

[0020] A third aspect of the present invention relates to a Kraft pulp comprising the microfibrillated cellulose according to the second aspect.

[0021] A fourth aspect of the present invention relates to a paper product comprising the microfibrillated cellulose according to the second aspect.

BRIEF DESCRIPTION OF DRAWINGS

[0022]

Fig. 1 shows the microscopic observation of microfibrillated cellulose produced from (a) high-yield kraft pulp (used in the present invention) and from (b) bleached Kraft pulp (used in the prior art) and from a (c) commercial microfibrillated cellulose from the prior art. The bar indicates the 100 um scale.

Fig. 2 shows the percentage of fines (based on the total sample, weighted in length, measured in a L&W Fiber Tester 912 equipment) of microfibrillated celluloses produced with different refining energies, from high-yield pulp (squares) and from unbleached pulp (diamonds) or bleached pulp (circles). The value of fines for a commercial microfibrillated cellulose is depicted by the solid line.

DETAILED DESCRIPTION AND DESCRIPTION OF PREFERRED EMBODIMENTS

[0023] It is here described a process for producing microfibrillated cellulose (also referred to in this description as MFC, for purposes of simplification) from a high-yield Kraft pulp, i.e., in the context of the present invention, a Kraft pulp with a total lignin content of 5% to 30% by weight, according to the description below which, surprisingly, simultaneously allows the production of microfibrillated cellulose with a lower energy consumption compared to, for example, from a conventional Kraft pulp (to which is associated, a low lignin content, i.e., in the context of the present invention, a total lignin content inferior to 5% by weight, and in which the microfibrillated cellulose obtained presents a papermaking ability that provides increased mechanical strength properties to the paper products incorporating it, in comparison with conventional solutions of the use of microfibrillated celluloses produced through conventional cellulose pulps, i.e., delignified by the typical chemical cooking processes, such as Kraft or sulfite, and/or additionally bleached.

[0024] In the context of the present invention, Kraft cooking process refers to Kraft cooking or sulfate cooking. It is a chemical process well known in the art which consists in cooking the wood in a cooking liquor usually consisting of sodium hydroxide and sodium sulfide, at temperatures of the order of 140 to 180 °C, in pressurized reactors. A conventional Kraft process is here understood as a typical chemical cooking process that yields a pulp production yield of about 45-55%.

[0025] In the context of the present invention, Kraft pulp refers to a pulp obtained by Kraft cooking.

[0026] In the context of the present invention, unbleached Kraft pulp refers to a pulp produced by the conventional Kraft process, typically with a total lignin content inferior to 5% by weight.

[0027] In the context of the present invention, bleached Kraft pulp refers to a pulp produced by the conventional Kraft process, and which is further subjected to a bleaching step, with a total lignin content typically inferior to 1 % by weight. The purpose of the bleaching step is to continue the delignification by the action of oxidizing agents, such as oxygen, chlorine dioxide and hydrogen peroxide.

[0028] In the context of the present invention, high-yield Kraft pulp refers to a Kraft pulp produced by a chemical Kraft cooking process with a yield of more than 60%, the pulp thus produced having a total lignin content of between 5% and 30% by weight. Therefore, when reference is made in this description to "high-yield Kraft pulp" it is meant as a simplified reference to a Kraft pulp with a total lignin content of 5 % to 30 % by weight.

[0029] In the context of the present invention, the cooking yield is calculated by the following formula:

$$\text{pulp weight/wood weight} \times 100$$

(Weights on an absolute dry basis)

[0030] In the context of the present invention, the total lignin content by weight is the sum of the contents of insoluble lignin (determined in accordance with the standard Tappi 222 om-02) and soluble lignin (determined in accordance with the standard Tappi UM 250 modified with the addition of borohydride for spectrophotometric measurement - Pinto P., Influência da estrutura química dos componentes da madeira no seu desempenho nos processes de produção de pastas celulósicas. Estudo comparative entre Eucalyptus globulus e outras folhosas, PhD Thesis, Universidade de Aveiro, 2005).

[0031] In the context of the present invention, and in accordance with the standard ISO/TS 20477, microfibrillated cellulose refers to cellulose fibres composed of, at least, one elementary fibre containing crystalline, paracrystalline and amorphous regions, with aspect ratio (length/diameter) superior to 10, and may contain longitudinal fibrils, crosslinking between particles or net-like structures, being produced by mechanical and/or chemical treatments of wood, such as enzymatic treatments, for example.

[0032] It is therefore common in the context of the technical field to designate the microfibrillated celluloses produced exclusively by mechanical treatments as "mechanical microfibrillated celluloses" and when produced through a combination of these with enzymatic treatments as "enzymatic microfibrillated celluloses", since, being chemically composed by the same elements as the raw material pulp, the intrinsic characteristics of the produced microfibrillated celluloses directly depend on the process used for their production, making it impossible to characterize them through their constituents due to their heterogeneous nature. This is also expected with other production methods and depending on the raw materials involved.

[0033] In the context of the present invention, percentage of fines refers to the percentage of fibrils with a length inferior or equal to 0.2 mm, measured on a L&W Fiber Tester 901 equipment, relative to the average length of the whole sample. With mechanical defibration technology it is possible to achieve 100% of fines, combining modern machinery and adequate energy and time consumption. However, in current state of the art industrial practice, it is common to treat the raw material to a level of fines close to 50% by weight (measurement carried out on a L&W Fiber Tester 912, length-weighted average). Depending on the intended use of the MFC, the content of fines to be achieved may be higher or lower.

[0034] In the context of the present invention, microfibrillated cellulose from high-yield Kraft pulp refers to microfibrillated cellulose produced from a high-yield Kraft pulp.

[0035] In the context of the present invention, microfibrillated cellulose from unbleached Kraft pulp refers to microfibrillated cellulose produced from an unbleached Kraft pulp.

[0036] In the context of the present invention, microfibrillated cellulose from bleached Kraft pulp refers to a microfibrillated cellulose produced from a bleached Kraft pulp.

[0037] In the context of the present invention, commercial microfibrillated cellulose refers to samples that can be purchased on the market with the characteristic of being produced from totally delignified wood pulp, after a conventional Kraft cooking (total lignin content in the cellulose fibre of the produced pulp inferior to 5% by weight), followed by a bleaching process to obtain the pulp that was finally used in the production of the microfibrillated cellulose by a mechanical process with an enzymatic pre-treatment.

[0038] In the context of the present invention, retention agent refers to an additive added during the paper formation in order to retain fines and mineral fillers, such as, but not limited to, a linear cationic polyacrylamide.

[0039] In the context of the present invention, containerboard refers to the paper commonly used to make corrugated boards. The top and bottom layer of a corrugated board is called linerboard. It is usually a two-layer product, a top layer and a base layer. Virgin and recycled fibre are used in the production of this type of paper. In the first option, when the fibre used is predominantly virgin fibre chemically produced by the Kraft method, the product is called kraftliner. When predominantly recycled fibres are used the product is referred to as a testliner. The fluting between two liners is called fluting or corrugated medium.

[0040] In the context of the present invention, a tissue paper refers to a paper used for hygienic and sanitary purposes, either at home or at public places.

[0041] A process for producing microfibrillated cellulose from a high-yield Kraft pulp is described herein, the latter comprising, by definition, a high lignin content, that is, in the context of the present invention, a total lignin content of 5 % to 30 % by weight.

[0042] Surprisingly, the process of the invention simultaneously allows the production of microfibrillated cellulose with a lower energy consumption in comparison with the processes of the prior art using conventional Kraft pulps (with a total lignin content inferior to 5% by weight) and where the microfibrillated cellulose obtained has a papermaking ability that provides increased mechanical strength properties to the paper products incorporating it, in comparison with conventional solutions using microfibrillated celluloses produced through conventional cellulose pulps (i.e., delignified by typical chemical cooking processes, such as Kraft or sulfite, and/or bleached).

[0043] In fact, and surprisingly, the process of the present invention makes it possible to produce microfibrillated cellulose, with the above-mentioned advantages, from Kraft pulps with a high total lignin content (from 5% to 30% by weight), contrary to the established practice in the prior art which discourages the use of such high total lignin content pulps, also commonly referred to as high-yield Kraft pulps.

[0044] The process described herein consists in the selection of a high-yield Kraft pulp followed by its mechanical defibration until a microfibrillated cellulose suspension is obtained. The process may also include, and prior to the mechanical defibration step, an enzymatic hydrolysis of the selected pulp.

[0045] According to a preferred embodiment of the first aspect of the present invention, the process further comprises, between the steps a) of selecting and b) of defibrating, a step of enzymatic hydrolyzing the pulp selected in step a).

[0046] According to a preferred embodiment of the first aspect of the present invention, in step a) the pulp is selected from the group consisting of hardwood pulp, softwood pulp and mixtures thereof.

[0047] According to a preferred embodiment of the first aspect of the present invention, in step a) the selected pulp is eucalyptus pulp.

[0048] According to a preferred embodiment of the second aspect of the present invention, the microfibrillated cellulose comprises a minimum content of fines of 15% by weight.

[0049] According to a preferred embodiment of the fourth aspect of the present invention, the paper product is selected from the group consisting of kraftliner paper, testliner paper, corrugated cardboard, paper for bags, paper for shopping bags, flexible packaging paper, tissue paper and printing and writing paper.

Examples

• *Process for the production of microfibrillated cellulose from high-yield eucalyptus Kraft pulp (CMF HYKEP)*

Example 1

[0050] In a conical refiner, high-yield eucalyptus Kraft pulp, with a total lignin content of 8 %, was previously disintegrated and subjected to refining, with the following refining parameters: rotation speed 1230 rpm, edge length 0,574 km/s, power 0,918 kW, SEL (specific energy load applied by the edge of the bars) 1,6 Ws/m and specific energy 350 kWh/ton. The resulting product was further refined in two phases in a disc refiner. The first phase was carried out with the refining parameters: rotation speed 700 rpm, edge length 39, 48 km/s, power 5,076 kW, SEL 0,15 Wm/s and specific energy 200 kWh/ton. The second phase was carried out with the refining parameters: rotation speed 700 rpm, edge length 39,48 km/s, power 5,922 kW, SEL 0,10 Wm/s and specific energy 250 kWh/ton. Refining was conducted until a minimum fines content of 15 % by weight (length weighted average, based on the total sample and determined on a L&W Fiber Tester 912 equipment) was reached.

[0051] Figure 1 depicts the microscopic analysis of the obtained microfibrillated cellulose suspensions. It was possible to verify the fibrillation obtained after mechanical treatment and the heterogeneity of sizes within the same sample. The samples were analyzed in a L&W Fiber Tester 912 equipment for particle size determination. Table 1 presents the length-weighted average of fibre lengths and diameters, as well as the degree of polymerization, calculated using the Mark Houwink equation (parameters and equation defined in Henrikson et al., Cellulose Nanopaper Structures of High Toughness, Biomacromolecules 2008, 9, 1579-1585) with the intrinsic viscosity values determined on the samples dissolved in cupriethylenediamine solutions, according to ISO 5351:2010.

Table 1. Characterization (dimensions and degree of polymerization) of microfibrillated celluloses produced from high-yield Kraft pulp used in the present invention and comparison with the values obtained for microfibrillated celluloses produced from unbleached pulp, bleached pulp and commercial microfibrillated cellulose from the prior art.

sample	% fines	Average length, mm	Average width, μm	Intrinsic viscosity, ml/g	Degree of polymerization
MFC - commercial bleached	26	0, 495	19,5	560	1333
MFC - bleached	32	0.369	28,3	1180	3724
MFC - unbleached	34	0.364	27,1	1080	3314
MFC - HYKEP	35	0,372	27,5	880	2531

[0052] Figure 2 depicts the percentage of fines (based on the total sample, weighted in length, measured on a L&W Fiber Tester 912 instrument) of microfibrillated cellulose produced with different refining energies.

[0053] It was possible to verify that, using the same refining energy, a higher percentage of fines was obtained with the high-yield Kraft pulp than with a Kraft pulp obtained by the conventional Kraft process (with a total lignin content of 2%), and than with the bleached pulp (with a total lignin content inferior to 1%), typically used in the previous technique. Thus, it was shown that with the high-yield pulp, a lower amount of energy was required to produce the same amount of fines.

Example 2

[0054] High-yield eucalyptus Kraft pulp, with a total lignin content of 5% by weight, was subjected to disintegration and refining as described in Example 1. The results obtained also showed that a higher percentage of fines, using the same refining energy, was obtained with this high-yield Kraft pulp than with a bleached Kraft pulp obtained by the conventional Kraft process.

Example 3

[0055] High-yield eucalyptus Kraft pulp, with a total lignin content of 10% by weight, was disintegrated and refined in a similar way as described in Example 1. A higher percentage of fines, for the same refining energy, was obtained with this high-yield Kraft pulp compared to a bleached Kraft pulp obtained by the conventional Kraft process.

Example 4

[0056] High-yield Kraft pulp from eucalyptus and pine in the ratio 85/15 by weight, respectively, with a total lignin content of 7% by weight, was subjected to disintegration and refining as described in Example 1. A higher percentage of fines, using the same refining energy, was also found with this high-yield Kraft pulp compared to a bleached Kraft pulp obtained by the conventional Kraft process.

Example 5

[0057] High-yield pine Kraft pulp, with a total lignin content of 30% by weight, was subjected to disintegration and refining as described in Example 1. A higher percentage of fines was also obtained with this high-yield Kraft pulp than with a bleached Kraft pulp obtained by the conventional Kraft process, in agreement with the previous examples.

• *Papermaking ability of microfibrillated cellulose from high-yield Kraft pulp*

[0058] After the production of MFC HYKEP, its papermaking ability was assessed, according to the following examples. The MFC HYKEP produced was added to a high-yield Kraft pulp (HYKEP) with a total lignin content of 7% by weight. However, this lignin content of the high-yield Kraft pulp to which MFC HYKEP is added is not linked to the corresponding content of the HYKEP pulp used for the production of MFC HYKEP. Any HYKEP pulp with a total lignin content of 5% to 30% by weight can be used.

Example 6 - *Comparison of the papermaking ability of microfibrillated cellulose obtained from high-yield eucalyptus Kraft pulp (MFC HYKEP) incorporated into high-yield eucalyptus Kraft pulp (HYKEP) in relation* to *the papermaking ability of microfibrillated cellulose obtained from bleached eucalyptus Kraft pulp (MFC BEKP) incorporated into bleached eucalyptus Kraft pulp (BEKP)*

[0059] High-yield eucalyptus Kraft pulp, at a consistency of 0.64% (volume/weight), was mixed with MFC HYKEP with a consistency of 0.5% (weight/weight) and 35% of fines, in proportions of 5 and 10% by weight.

[0060] Bleached eucalyptus Kraft pulp (BEKP), with a total lignin content inferior to 1% by weight, at a consistency of 0.64% (volume/weight) was blended with MFC BEKP with a consistency of 0.5% (weight /weight) and 31, 45 or 54% of fines, in proportions of 5 and 10% by weight.

[0061] Isotropic laboratory sheets were prepared on a bench sheet former. For this, the pulps were previously refined. The MFC suspension was added to the refined pulp suspension, in a beaker, and subjected to magnetic stirring for 120 s, time after which the mixture was poured into the sheet former, following the ISO 5269-1 standard for sheet formation.

◦ Results

Structural properties and mechanical strength properties of 150 g/m^2 (135 $g_{over\ dry\ (OD)}$/m^2) sheets

[0062] Tables 2 and 3 show the comparative results of the relative increases in the mechanical strength properties compared to the references of sheets produced from BEKP pulp without MFC BEKP and sheets produced from HYKEP pulp without the addition of CMF HYKEP. The mechanical properties were measured according to the corresponding standards: burst index (ISO 2758:2015), tear index (ISO 1974:2012, tensile index (ISO 1924-2:2008), Scott-Bond (TAPPI 403).

Table 2. Increases in strength properties (%) obtained in sheets with 5% MFC incorporation, relative to the references (without MFC) .

	MFC BEKP 31% fines	MFC BEKP 45% fines	MFC BEKP 54% fines	MFC HYKEP 35% fines
Incorporation of MFC	5%	5%	5%	5%
Burst index	24	24	36	43
Tear index	3	5	2	22
Tensile index	8	10	16	31
Scott-Bond	90	45	77	104

Table 3. Increases in strength properties (%) obtained in sheets with 10% MFC incorporation, relative to references (without MFC) .

	MFC BEKP 31% fines	MFC BEKP 45% fines	MFC BEKP 54% fines	MFC HYKEP 35% fines
Incorporation of MFC	10%	10%	10%	10%
Burst index	38	39	52	89
Tear index	5	6	6	28
Tensile index	22	19	28	70
Scott-Bond	124	103	130	128

[0063] It is possible to verify an increase in the burst, tear and tensile indexes for HYKEP pulp sheets with MFC HYKEP in relation to the reference (HYKEP pulp sheets without MFC) . This increase is also higher than the increase observed for BEKP pulp sheets with MFC BEKP in relation to the corresponding reference (BEKP pulp sheets without MFC).

[0064] It is thus verified the effect of obtaining increased mechanical strength properties in sheets constituted by HYKEP pulp and MFC HYKEP in relation to the conventional option of adding MFC BEKP to BEKP pulp.

[0065] Increased burst, tear and tensile indexes for HYKEP pulp sheets with MFC HYKEP over reference (HYKEP pulp sheets without MFC) were also observed with MFC HYKEP with 15% and 50% of fines by weight.

Example 7 - Comparison of the papermaking ability of microfibrillated cellulose obtained from high-yield eucalyptus Kraft pulp (MFC HYKEP) or from commercial microfibrillated cellulose (MFC commercial) (white) incorporated into high-yield eucalyptus Kraft pulp (HYKEP)

[0066] 135 g/m^2 (OD) sheets were prepared from high-yield eucalyptus Kraft pulp at a consistency of 0.64% (volume/-weight) mixed with MFC HYKEP at a consistency of 0.5% (weight/weight). The procedure for forming the sheets was the same as in the previous example.

◦ Results

Mechanical strength properties of 150 g/m^2 (135 g_{OD}/m^2) sheets

[0067] Table 4 depicts the results for the mechanical strength properties of 150 g/m^2 sheets made from HYKEP pulps with different proportions of CMF HYKEP and of 150 g/m^2 sheets made from HYKEP pulp without the addition of CMF HYKEP. Additionally, a comparison with the same results obtained with the addition of white commercial MFC to HYKEP pulp is also presented.

Table 4. Increases in strength properties (%) relative to the reference (HYKEP without MFC HYKEP).

	MFC commercial		MFC HYKEP	
Incorporation of MFC	5%	10%	5%	10%
Burst index	6	15	12	19
Tear index	8	15	15	11
Tensile index	7	12	5	15
Tensile index (humidity=54%)			76	40
Scott-Bond	3	28	25	35

[0068] Incorporating 5 and 10% by weight of CMF HYKEP 35% fines increases the mechanical strength of the sheets, such as burst index, tear index and tensile index. The increases observed for CMF HYKEP are always higher than the corresponding increases with commercial CMF.

[0069] Increases in the sheet mechanical strength such as burst index, tear index and tensile index were also observed with CMF HYKEP with 15% and 50% of fines by weight.

Example 8 - Comparison of the papermaking ability of microfibrillated cellulose obtained from high-yield eucalyptus Kraft pulp (MFC HYKEP) incorporated to high-yield eucalyptus Kraft pulp (HYKEP) with and without retention agent

[0070] Sheets of 135 g/m^2 (OD) were prepared from HYKEP pulp and at a consistency of 0.64% (volume/weight) mixed with MFC HYKEP with a consistency of 0,5 % (weight/ weight). An additional series was produced with the addition of a retention agent according to the compositions shown in Table 5.

[0071] The procedure for forming the sheets was the same as in the previous examples.

Table 5. Compositions used in the preparation of the 135 g/m^2 sheets.

Sheets 135 g/m^2 (OD)			
	HYKEP	MFC HYKEP 35% fines	Retention agent
Consistency	0, 6	0,5	0, 025
% of incorporation into the sheet	90 e 95	0, 5 e 10	0 e 0,014

[0072] Table 6 shows the comparative results for the mechanical strength properties of 150 g/m^2 sheets from pulps containing HYKEP pulp with different proportions of MFC HYKEP and of 150 g/m^2 sheets from HYKEP pulp without MFC HYKEP addition. Two series are presented, namely in the absence and presence of a retention agent (linear cationic polyacrylamide).

Table 6. Increases in strength properties (%) relative to the reference (HYKEP without MFC HYKEP) in the presence and absence of a retention agent.

	without retention agent		with retention agent	
Incorporation of MFC	5%	10%	5%	10%
Burst index	12	19	43	89
Tear index	15	11	22	28
Tensile index	5	15	31	70
Tensile index (humidity=54%)	76	40	3	7
Scott-Bond	25	35	104	128

[0073] The incorporation of 5 and 10% by weight of MFC HYKEP 35% fine originated an increase in the mechanical strength properties in relation to the reference, both in the presence and in the absence of a retention agent (always positive results in table 4). Additionally, it was observed that in the presence of the retention agent the papermaking ability of MFC HYKEP is enhanced (increase relative to the reference without MFC higher than the one observed without retention agent).

[0074] Increases in mechanical strength properties over the reference, both in the presence and absence of a retention agent, were also observed with MFC HYKEP with 15% and 50% of fines by weight.

Example 9 - Comparison of the papermaking ability of microfibrillated cellulose obtained from high-yield eucalyptus Kraft pulp (MFC HYKEP) incorporated to high-yield eucalyptus Kraft pulp (HYKEP) with and without cationic starch.

[0075] 135 g/m^2 (OD) sheets were prepared from HYKEP pulp, with cationic starch incorporated and at a consistency of 0.64 % (volume/weight) mixed with MFC HYKEP with a consistency of 0.5 % (weight/weight) and with a retention agent according to the compositions shown in Table 6.

[0076] The procedure for forming the sheets was the same as in the previous examples.

Table 7. Compositions used in the preparation of the 135 g/m^2 sheets.

135 g/m^2 (OD) sheets				
	HYKEP	Cationic starch	MFC HYKEP 35% fines	Retention agent
Consistency	0, 6	0, 6	0,5	0, 025
% of incorporation into the sheet	90 e 95	1	0, 5 e 10	0 e 0,014

◦ Results

Structural properties and mechanical strength properties of 150 g/m² (135 g_{OD}/m^2) sheets

[0077] Table 8 shows the comparative results for the mechanical strength properties of 150 g/m² sheets from HYKEP pulps with different proportions of MFC HYKEP and 150 g/m² sheets from HYKEP pulp without addition of MFC HYKEP, with and without starch and with and without a retention agent.

Table 8. Increases in strength properties (%) relative to the reference (HYKEP without MFC), in the presence and absence of bulk starch (added to the pulp suspension) and also in the presence of the retention agent.

	Without starch		with starch		with starch and retention agent	
Incorporation of MFC	5%	10%	5%	10%	5%	10%
Drainability, °SR	48	114	88	175	45	75
Burst index	12	19	12	47	6	24
Tear index	15	11	-6	-1	-1	-5
Tensile index	5	15	0	26	6	25
Scott-Bond	25	35	16	65	33	64

[0078] The use of paper additives commonly used in paper material production, such as cationic starch and retention agents, keeps the competitive advantage of using MFC HYKEP for strengthening the mechanical properties.

[0079] The competitive advantage of using MFC HYKEP for strengthening properties was also observed with MFC HYKEP with 15% and 50% of fines by weight.

Example 10 - Comparison of the papermaking ability of microfibrillated cellulose obtained from high-yield eucalyptus Kraft pulp (MFC HYKEP), with 35 or 41% fines, added to high-yield eucalyptus Kraft pulp (HYKEP)

[0080] Sheets 135 g/m² (OD) were prepared from HYKEP pulp, with incorporated cationic starch and at a consistency of 0,64 % (volume/weight) mixed with MFC HYKEP produced with a fines content of 35 or 41 %, with a consistency of 0,5 % (weight/weight) in the presence and absence of a retention agent.

[0081] The procedure for forming the sheets was the same as in the previous examples.

◦ Results

Mechanical strength properties of 150 g/m² (135 g_{OD}/m^2) sheets

[0082] In Table 9 and 10, the increases in mechanical strength properties of HYKEP pulps with incorporation of MFC HYKEP with different levels of fines were compared with the properties of the sheets constituted by high-yield pulp without the addition of MFC HYKEP.

Table 9. Increases in the strength properties (%) relative to the reference (HYKEP without MFC), in the presence of bulk starch and in the absence of the retention agent, of the strength properties of sheets with the addition of 5 % HYKEP CMF with 35 or 41 % of fines.

	Without retention agent	
	MFC 35% fines	MFC 41% fines
	5%	5%
Burst index	12	30
Tear index	-6	21
Tensile index	0	14
Scott-Bond	16	79

Table 10. Increases in the strength properties (%) relative to the reference (HYKEP without MFC), in the presence of bulk starch and in the presence of the retention agent, of the strength properties of sheets with the addition of 5 or 10 % MFC HYKEP with 35 or 41 % of fines.

	With retention agent			
	MFC 35% fines		MFC 41% fines	
	5%	10%	5%	10%
Burst index	6	24	15	48
Tear index	-1	-5	12	12
Tensile index	6	25	20	44
Scott-Bond	33	64	41	75

[0083] As expected, the MFC HYKEP with higher fines content had a more pronounced effect on the strength properties, for example with a 50 % increase in the burst index when compared to the reference without MFC HYKEP.

Claims

1. A process for the production of microfibrillated cellulose wherein the process comprises the steps of:

a) selecting a Kraft pulp with a total lignin content of 5 % to 30 % by weight;
b) mechanically defibrating the pulp selected in step a) until obtaining a microfibrillated cellulose suspension with a minimum fine content of 15% by weight.

2. The process according to claim 1, wherein the process further comprises, between the steps a) of selecting and b) of mechanically defibrating, a step of enzymatic hydrolyzing the pulp selected in step a).

3. The process according to any of the preceding claims, wherein in step a) the pulp is selected from the group consisting of hardwood pulp, softwood pulp and mixtures thereof.

4. The process according to claim 3, wherein in step a) the selected pulp is eucalyptus pulp.

5. A microfibrillated cellulose obtainable by the process as claimed in any of claims 1 to 4.

6. The microfibrillated cellulose according to claim 5, wherein the microfibrillated cellulose comprises a minimum content of fines of 15% by weight.

7. A Kraft pulp comprising the microfibrillated cellulose claimed in any of claims 5 and 6.

8. A paper product comprising the microfibrillated cellulose claimed in any of claims 5 and 6.

9. The paper product according to claim 8, wherein the paper product further comprises a retention agent.

10. The paper product according to any of claims 8 and 9, wherein the paper product is selected from the group consisting of kraftliner paper, testliner paper, corrugated cardboard, paper for bags, paper for shopping bags, flexible packaging paper, tissue paper and printing and writing paper.

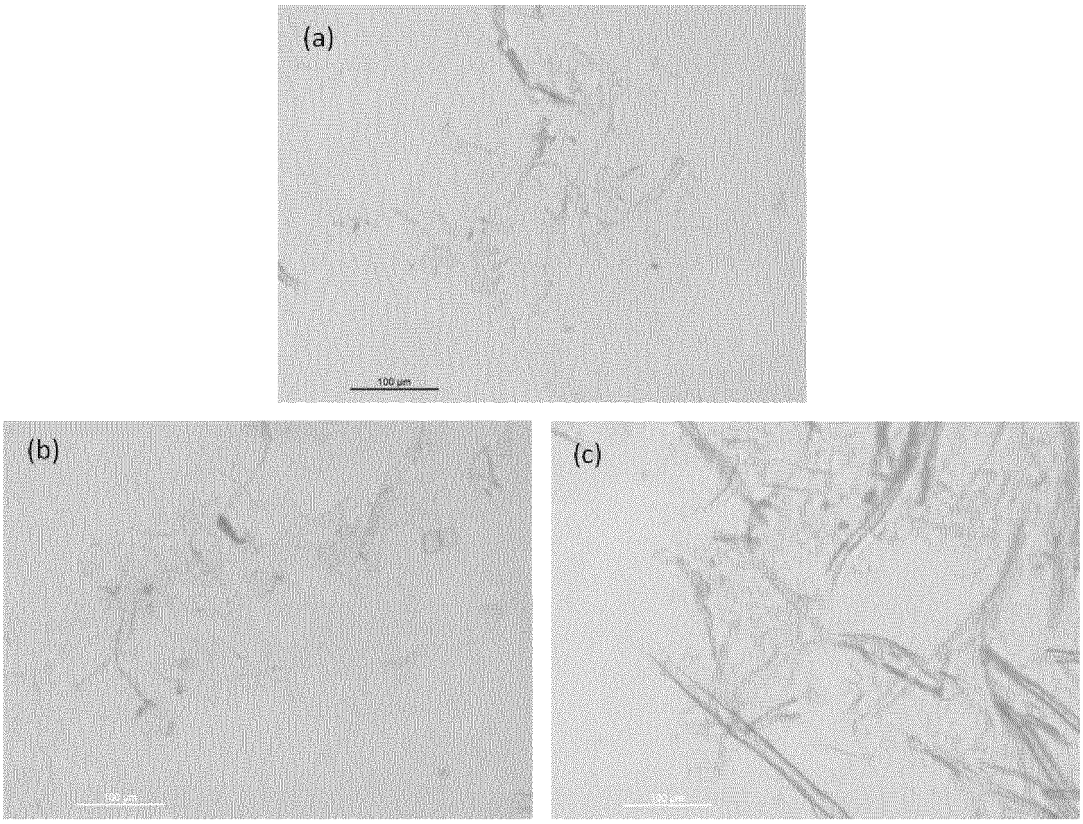

Figure 1

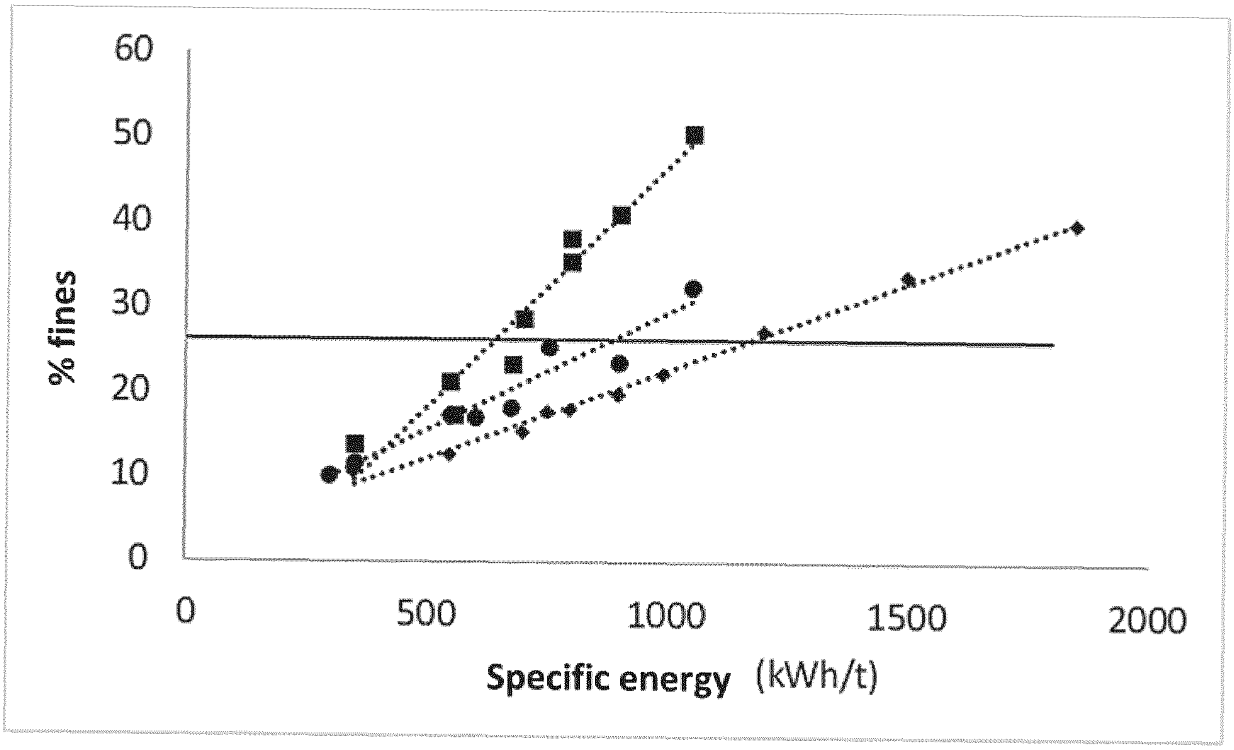
60
50
40
30
20
10
0
% fines
0
500
1000
1500
2000
Specific energy (kWh/t)

Figure 2

RELATÓRIO DE PESQUISA INTERNACIONAL

Pedido internacional Nº
PCT/IB2023/052806

A. CLASSIFICAÇÃO DO OBJETO

D21H 11/08(2006.01)i

De acordo com a Classificação Internacional de Patentes (IPC) ou com a classificação nacional e IPC

B. DOMÍNIOS ABRANGIDOS PELA PESQUISA

Documentação mínima pesquisada (sistema de classificação seguido pelo símbolo da classificação)

D21H

Documentação adicional pesquisada, além da mínima, na medida em que tais documentos estão incluídos nos domínios pesquisados

Base de dados eletrônica consultada durante a pesquisa internacional (nome da base de dados e, se possível, termos usados na pesquisa)

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C. DOCUMENTOS CONSIDERADOS RELEVANTES

Categoria*	Documentos citados, com indicação das partes relevantes, se apropriado	Relevante para as reivindicações Nº
X	TARRÉS QUIM ET AL. "Evaluation of the fibrillation method on lignocellulosic nanofibers production from eucalyptus sawdust: A comparative study between high-pressure homogenization and grinding" *INTERNATIONAL JOURNAL OF BIOLOGICAL MACROMOLECULES, ELSEVIER BV, NL,* Vol. 145, 11 de Novembro de 2019 (2019-11-11), páginas 1199-1207, [recuperado no dia 2019-11-11] DOI: 10.1016/J.IJBIOMAC.2019.10.046 ISSN: 0141-8130, XP086012931 parágrafo [2.1.] - parágrafo [2.5.]; figura 1 parágrafos [2.7.], [2.8.], [3.1.]; figura 4; tabelas 2,3	1-10
X	HERRERA MARTHA ET AL. "Preparation and evaluation of high-lignin content cellulose nanofibrils from eucalyptus pulp" *CELLULOSE, SPRINGER NETHERLANDS, NETHERLANDS,* Vol. 25, Nº 5, 09 de Abril de 2018 (2018-04-09), páginas 3121-3133, [recuperado no dia 2018-04-09] DOI: 10.1007/S10570-018-1764-9 ISSN: 0969-0239, XP036497570 página 3122, coluna 2, parágrafo 3 - página 3123, coluna 2, parágrafo 2	1-10

☐ Outros documentos estão listados na continuação do Quadro C.

☐ Ver o anexo relativo à família de patentes

* Categorías especiais dos documentos citados:

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- "&" documento membro da mesma família de patentes

Data da conclusão da pesquisa internacional	Data do envio do relatório de pesquisa internacional
27 de Junho de 2023	**10 de Julho de 2023**

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Nº de telefone:

Formulário PCT/ISA/210 (segunda folha) (Janeiro 2015)

REFERENCES CITED IN THE DESCRIPTION

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- **CHAKER et al.** Key role of the hemicellulose content and the cell morphology on the nanofibrillation effectiveness of cellulose pulps. *Cellulose*, 2013, vol. 20, 2863-2875 **[0015]**
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