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(54) SEMI-BLEACHED OR UNBLEACHED EUCALYPTUS GLOBULUS PULP FOR TISSUE PRODUCTS

(57) The present invention relates to a semi-bleached or unbleached *Eucalyptus globulus* pulp, the use of which for the production of tissue products allows the development of key properties of such products, such as bulk, strength, absorption, softness and even of a visual perception for consumers of sustainable and environmentally friendly products.

The invention disclosed herein also includes the use of semi-bleached or unbleached *Eucalyptus globulus* pulp for the production of tissue products, tissue paper sheets incorporating semi-bleached or unbleached *Eucalyptus globulus* pulp and their use for the production of toilet paper, napkins and kitchen rolls.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to semi-bleached or unbleached *Eucalyptus globulus* pulp and to its use for the production of tissue products. Additionally the present invention further relates to tissue papers sheets made by incorporating semi-bleached or unbleached *Eucalyptus globulus* pulp, and their use for the production of household and sanitary products.

BACKGROUND OF THE INVENTION

[0002] Tissue papers are those used both domestically and in public spaces for hygienic and sanitary use. A tissue paper product is characterized by different key properties, namely bulk, strength, absorption, softness and even visual appearance. The consumer of this type of product seeks a positive balance in terms of the overallity of these different properties. In addition, the current consumer also intends to purchase environmentally conscious products produced through raw materials and processes that lead, for example, to lower chemical and water consumptions.

[0003] The document JP2005325493 discloses a tissue paper for kitchen applications produced with unbleached pulp of a coniferous wood, with improved whiteness. This is achieved through the use of ultraviolet light absorption compounds and an antioxidant compound. EP0416278B1 discloses a tissue paper produced using unbleached sulfate pulp. This solution only allows improvements in softness and tensile strength, without any mention of bulk characteristics and absorption capacity.

[0004] CN102733225A relates to an ecologic and environmentally friendly toilet paper making process which uses unbleached pulp and additionally includes fermentation processes. The characteristics of the paper produced are softness, fineness, durability and a natural fiber fragrance.

[0005] Therefore, there is a need for tissue paper products with a globally improved consumer-appreciated paper properties such as bulk, absorbency, capillarity, strength, softness and consumer-friendly visual appearance of the use of an environmentally sustainable product, produced using existing processes in the industrial pulp and paper production units and with the raw materials commonly used therein, with lower environmental impact and production costs as, for example, on the consumption of chemical additives and water. Such a problem is solved by the invention described herein.

SUMMARY OF THE INVENTION

[0006] The semi-bleached or unbleached *Eucalyptus globulus* pulps disclosed in this document unexpectedly enables the production of tissue paper products with a range of improved consumer-appreciated paper properties, such as bulk, absorbency, capillarity, strength, softness and consumer-identifying visual appearance of the use of an environmentally sustainable and friendly product.

[0007] Additionally, is advantageously produced using processes already in place at pulp and paper mills, and the raw materials commonly used therein, with a lower impact on the environment and production costs as regards, for example, to the consumption of chemical additives and water.

[0008] An example of the most commonly used industrial processes for pulp production is the kraft process, or sulfate process, in which wood chips are treated at a temperature of around 145-155 °C with the white liquor, consisting essentially of sodium hydroxide (NaOH) and sodium sulfide (Na_2S). Normal values for the alkali load, the amount of active alkali, in kg Na_2O, required to ensure a correct delignification, range between 2300 and 2500 kg Na_2O per cooking procedure.

[0009] The invention here disclosed describes a cellulose pulp for the production of tissue paper products comprising semi-bleached or unbleached *Eucalyptus globulus* fibers.

[0010] According to the invention described herein, the semi-bleached or unbleached *Eucalyptus globulus* pulp comprises fibers having a length of not less than 0.8 mm, a width of not less than 19 μm and a coarseness of not less than 6 mg/100m. The semi-bleached or unbleached *Eucalyptus globulus* pulp *presents* a viscosity of not less than 1300 mL/g and a carboxyl content of not less than 10%.

[0011] The present disclosure further includes tissue paper sheets incorporating at least 35% of the semi-bleached or unbleached *Eucalyptus globulus* pulp, and short and long cellulose bleached fiber pulps. The paper sheets have globally improved paper properties compared to tissue paper sheets that incorporate only bleached pulps into their composition. The paper sheets have bulk values greater than 1 cm^3/g, preferably from 2 to 7 cm^3/g and a tensile index greater than 4 kN.m/kg, preferably from 6 to 60 kN.m/kg, an absorption capacity greater than 7 gH_2O/g_{paper}, preferably from 7 to 10 gH_2O/g_{paper}, an air permeability greater than 450 $L/m^2/s$, preferably from 500 to 1090 $L/m^2/s$, and a softness greater than 50 HF, more preferably from 55 to 80 HF.

[0012] The tissue paper sheets disclosed have a tear index greater than 6 $mN.m^2/g$, more preferably from 6 to 10

mN.m^2/g, a burst index greater than 1 kPa.m^2/g, preferably from 1 to 4 kPa.m^2/g, a capillarity of not less than 60 mm/10min, and an opacity greater than 70%, preferably greater than 90%.

[0013] The invention disclosed herein thus includes the use of the semi-bleached or unbleached *Eucalyptus globulus* pulp for the production of tissue products and the use of tissue papers sheets, incorporating the semi-bleached or unbleached *Eucalyptus globulus* pulp, for the production of household and sanitary products, such as toilet paper, napkins, kitchen paper rolls and tissues.

[0014] In the production process of tissue products, the described pulp can be used in different forms, such as in the form of dried pulp bales and in the form of a slush, the later feed to the industrial process through pipeline systems.

DETAILED DESCRIPTION OF THE INVENTION

1. Biometric characterization

[0015] The biometric analysis of the fibers was performed in a Fiber Tester equipment (Lorentzen & Wettre), which is an instrument for advanced fiber analysis. The equipment measures, by 2D image analysis, a wide variety of properties such as length, width, fines content, coarseness, among others. Coarseness is defined as the weight per unit length of fiber expressed in milligrams per 100 meters. For that, 1 g (dry basis) of pulp was dispersed in 1 L of distilled water. Subsequently, all the suspensions were positioned for analysis by the equipment using available software. For each pulp three measurements were made, the final value of each parameter resulting from the arithmetic mean of the values obtained at the three measurements.

2. Chemical characterization

a. Extractable compounds content

[0016] Extractable compounds are hydrophobic (lipophilic) components present in wood and extracted by organic solvents.

[0017] The extractable compounds content was determined using ethanol/toluene in quantities enough for samples analysis preparation, as it requires a pulp pre-extraction. The extraction was carried out during approximately 4 hours (24 extraction cycles) of 2 g (dry basis) of pulp in a 100 mL capacity Soxhlet extraction apparatus, using 250 mL of a 1:2 (v/v) ethanol/toluene solution. The insoluble residue was filtered and washed with hot absolute ethanol, for removing any remaining toluene, and dried at room temperature, contrary to what is indicated at the standard TAPPI T 204 om-88, since washing with water, as described, could lead to the loss of pentosans and other polysaccharides of low molecular weight. The obtained extract was dried at a rotary evaporator equipment and the extractable content was determined gravimetrically.

b. Pentosans content

[0018] Pentosans content was determined according to the Tappi Test Method T 223 cm-10. This method is based on the action of hydrochloric acid on the pulp hemicelluloses, hydrolyzing them and, consequently, converting the xylose and other pentoses to furfural, which is collected with the distillate and, reacting with orcinol, forms a colored complex making therefore possible the content quantification by spectrophotometry.

[0019] About 0.5-1.0 g (dry basis) of unbleached pulp pre-extracted in ethanol/toluene (1:2), together with 20 g of NaCl and 100 mL of HCL 3.85 N, was inserted into a distillation flask. In a hopper, 250 mL of 3.85 N HCl was added and the acid distillation was started into a volumetric flask placed in an ice bath.

[0020] Finally, 5 mL of the distillate was pipetted, 25 mL of the orcinol ferric chloride reagent was added, and the mixture was kept in a thermostatic bath for 1 hour. Absolute ethanol was added and the volumetric flask was placed again in the thermostatic bath for another hour. The solution absorbance at 630 nm was then read, and measurements comparisons were carried out using a 5 mL blank of 3.85 N HCl.

[0021] The pentosans content was obtained with the aid of the calibration curve and equations presented below:

$$m_{xylan}\,(mg) = 0{,}88 \times m_{xylose}\,(mg)$$

$$Pentosans\ content\ \ (\%) = \frac{m_{pentosans\ in\ each\ sample}}{10 \times w}$$

where w is the dry weight (g) of the sample.

c. Carboxyl content

[0022] The content of carboxyl groups was determined according to the TAPPI T 237 om-93 standard method. About 2.5 ± 0.1 g of disintegrated pulp was first weighed and 250 mL of a diluted hydrochloric acid solution (approximately 0.1 M) was added during 12 hours, ensuring that all existing carboxylic groups are in their protonated form. Subsequently, the pulp was filtered and washed with distilled water until the pH of the filtrate equaled the pH of the distilled water. To the pulp it was added 50 mL of an aqueous sodium bicarbonate-sodium chloride solution, the resulting mixture stirred for about 5 hours, filtered, and the filtrate twice titrated (25 mL in each titration) with a standard solution of hydrochloric acid (0.01 M) using methyl red as indicator. At the first color change the solution was boiled for 1 minute to release CO_2. Titration is resumed ending only when the solution changes to pink. The blank was prepared by titrating 25 mL of sodium bicarbonate-sodium chloride solution with 0.01 M HCl. The content of carboxyl groups was determined with the following equation:

$$Content\ COOH\ \left(\frac{mmol}{100\ g}\right) = \left(b - a - \frac{C_w \times a}{50}\right) \times \left(\frac{50}{25 \times w}\right)$$

where a is the volume, in mL, of hydrochloric acid (0,01 M) spent during titration, b is the volume, in mL, of hydrochloric acid (0,01 M) consumed during the blank titration, C_w is the mass, in g, of the water in the pulp after filtration, and w is the weight, in g, of the dry pulp.

d. Pulp viscosity

[0023] The viscosity was determined according to the SCAN-test standards SCAN-CM 15:88, which consists on the determination of the viscosity of pulps by solubilization in a dilute copper-ethylenediamine (CED) solution.

[0024] The pulp sample was reduced to small fragments in the amount indicated at the table provided by the method (Table 7, Annex C.1.) - 150 mg of pulp were weighed. Each sample was placed into a glass vial along with 25 mL of distilled water and some copper wires. The vials were then placed on a shaker for as long as necessary to ensure that the pulp was completely disintegrated. The procedure continued with adding 25 mL of 1 M CED solution, expelling all existing air and stirring until the sample is completely dissolved. Finally, the temperature of the viscometer bath and the sample's were adjusted to 25.0 ± 0.1 °C and, with the aid of a syringe, a portion of the solution was aspirated and allowed to flow unobstructed. The time it takes to travel the distance between the two viscometer marks was measured to within ± 0.2 s. At least 5 readings were taken for each sample.

[0025] With the flow time of each sample, t_n, it is possible to calculate its relative viscosity, η_{rel}, through the relationship shown in the equation:

$$\eta_{rel} = h \times t_n$$

where h represents the viscometer constant, obtained from the equipment calibration. From the table provided by the aforementioned standard, it is possible to read the value resulting from multiplying the viscosity value with the pulp concentration, $[\eta]C$.

[0026] Biometric and chemical measurements and comparisons were carried out for an unbleached *Eucalyptus globulus* pulp (**UBP**), for a bleached short cellulose fiber pulp (**SF**), and for a bleached long cellulose fiber pulp (**LF**).

3. Preparation of paper sheets

[0027] Tissue paper sheets with a weight of 20 g/m^2, and not subjected to any pressing procedure, were prepared following an adaptation of the standard method ISO 5269-1:2005. Additionally, 60 g/m^2 tissue paper sheets were prepared according to the same ISO.

[0028] The pulps described above, **SF**, **LF** and **UBP** were used. The prepared formulations are described in Table 1. Reference formulations (**REF 1** and **REF 2**) consist on formulations used in the production of tissue paper sheets. The other formulations were based on the replacement of short fibers content by unbleached pulp (**UBP 1** to **UBP 4**).

Table 1. Formulations used in sheet preparation

	Percentages (%) (w/w)					
	References		Formulations with UBP			
Formulations	REF 1	REF 2	UBP 1	UBP 2	UBP 3	UBP 4
SF	70	100	35	20	-	-
LF	30	-	30	30	30	-
UBP	-	-	35	50	70	100

[0029] The same formulations were tested with refined pulps having a Schopper degree of 25/26 °SR (measured by the Schopper-Riegler method, which provide a measure of the rate at which a dilute suspension of pulp may be dewatered). For that, the dried pulps were disintegrated individually, the pH was adjusted to 7-7.5, and finally refined in a PFI refiner according to the standard ISO 5264-2. The Schopper degree, °SR, was again confirmed after preparation of the formations indicated in Table 1, standard ISO 5267-1:1999.

[0030] The prepared sheets were stored according to the standard ISO 187:1990 for further analysis.

4. Paper properties of 20 g/m^2 tissue paper sheets

[0031] The 20 g/m^2 sheets were analyzed as indicated in Table 2.

Table 2. Paper properties analyzed for sheets of 20 g/m^2 and respective measure standards.

Property	Standard
Weight	ISO 12625-6:2005
Bulk	ISO 12625-3:2014
Dry tensile index	ISO 12625-4:2005
Klemm capillarity	ISO 8787-1986
Absorption capacity	Adaptation 12625-8:2010

[0032] The softness was analyzed on an Emtec TSA - Tissue Softness Analyzer. This device combines data from the three parameters that have the greatest influence on the human feel to the touch: fibers softness, smoothness and sheet stiffness. The calculation method used by the device is an algorithm that calculates the hand feel (HF).

[0033] The water absorption of the tissue papers was determined according to the standard ISO 12625-8:2010, by the immersion absorption method. Approximately 2 g of paper was placed in a basket of certain dimensions, contrary to what is mentioned at the standard, which indicates the use of 5 g of paper.

5. Paper properties of 60 g/m^2 tissue paper sheets

[0034] The prepared 60 g/m^2 sheets were analyzed as indicated in Table 3.

Table 3. Paper properties analyzed for sheets of 60 g/m^2 and respective measure standards.

Property	Standard
Weight	ISO 536:2012
Bulk	ISO 534:2011
Tensile index	ISO 1924-2
Burst index	ISO 2758:2014
Extension	ISO 1924-2:2008
Tear Index	ISO 1974:2012
Opacity	ISO 2471

(continued)

Property	Standard
Gurley air resistance	ISO 5636-5:2013
Capillarity	NP686:1990

[0035] Additionally, a Scott Test was carried out and the Gurley's air resistance was measured.

[0036] Mechanical strength properties of pulp furnishes ultimately contribute to the strength characteristics of the out coming material, as paper sheets are subjected to considerable stresses during processing and use. The Scott Test is related to the internal fibers bonding strength of the paper when subjected to delamination. It allows the determination of the energy (or force) required to delaminate a sheet of paper in the z-direction. In this method (TAPPI T 569 standard) the paper sheet is delaminated under the action of a pendulum of controlled mass and velocity. The internal strength of the fibers is affected by the paper sheets formation (bonding between layers) and also by the process of pulp refining.

[0037] The Gurley's air resistance is a structural property that quantifies the time required for a certain volume of air (100 mL) to pass through a given area of paper under constant pressure, ISO 5636-5:2013 standard. It is an indirect measure of the porosity of the fibrous matrix.

[0038] Both tests were performed under the same atmospheric conditions used for sample conditioning and sample preparation (T = 23 °C ± 1 °C and Relative Humidity (RH) = 50% ± 2%, according to the ISO 187:1990 standard.

Examples

a. Biometric and Chemical Properties

[0039] The biometric properties of the pulps, **SF**, **LF** and **UBP**, were analyzed, with and without refining, and the results are depicted in Table 4.

Table 4. Biometric properties of the unrefined and refined pulps.

	SF	**SF**	**LF**	**LF**	**UBP**	**UBP**
PFI rotations	0	1000	0	5500	0	400
Fiber Length, mm	0.79 ± 0.00	0.79 ± 0.00	2.15 ± 0.01	2.07 ± 0.00	0.82 ±0.00	0.82 ± 0.00
Fiber Width, μm	18.6 ± 0.1	18.3 ± 0.00	32.4 ± 0.1	32.3 ± 0.1	19.3 ± 0.00	19.3 ± 0.00
N. ° Fibers/g, $\times 10^{-6}$	18.7 ± 0.1	18.2 0±.22	4.30 ± 0.07	2.9 ± 0.0	18.2 ± 0.3	17.7 ± 0.1
Coarseness, mg/100m	6.3 ± 1.20	6.94 ± 0.11	15.1 ± 0.4	16.56 ± 0.05	6.7 ± 0.1	6.86 ± 0.04
Fines (0,0-0,200 mm), %	4.2 ± 0.1	4.3 ± 0.0	5.7 ± 0.1	5.4 ± 0.01	3.9 ± 0.1	3.7 ± 0.1
Shape, %	90.7 ± 0.1	92.50 ± 0.36	88.2 ± 0.07	90.80 ± 0.08	93.97 ± 0.05	92.60 ± 0.00
Curl, %	9.2 ± 0.1	8.1 ± 0.4	13.4 ± 0.1	10.1 ± 0.1	6.4 ± 0.1	8.0 ± 0.0
Mean kink index	1.3 ± 0.0	1.04 ± 0.15	0.90 ± 0.00	0.71 ± 0.02	0.74 ±0.00	0.98 ± 0.01

[0040] Observing the results obtained, it is verified that the fiber length values are within the expected. The fibers **UBP** have larger width values than the other short fibers. The fibers **UBP** also present higher values than the other short fibers with regard to coarseness. Comparing unrefined pulps and after refining pulps, it is verified that the biometric properties of the fibers did not change significantly.

[0041] The results of the chemical characterization of the pulps under study are shown in Table 5.

Table 5. Chemical properties of the pulps **SF**, **SF** and **UBP**.

	SF	LF	UBP
Viscosity, mL/g	716 ± 3	699 ± 14	1306.4 ± 1.9
Carboxylic, %	7.03 ± 0.05	8.92 ± 0.23	13.52 ± 0.37
Pentosans, %	19.6 ± 0.25	8.1 ± 0.02	15.54 ± 0.49

(continued)

	SF	LF	UBP
Extractable, %	0.21 ± 0.00 *	0.40 ± 0.22 *	0.37 ± 0.03**

*Extractable in acetone
**Extractable in ethanol:toluene(1:2)

[0042] A good degree of cellulose polymerization is maintained for the fibers of the **UBP** pulp, as inferred by its higher viscosity value than that of **SF**. The pulp **UBP** also has a higher percentage of carboxyl content than the other pulps.
[0043] The pentosans content (measured by the xylan content, the majority of hemicelluloses in short fiber pulps) is within the typical range for this type of short fiber *Eucalyptus globulus* pulp.

b. Unrefined pulps

i. Paper properties - 20 g/m^2 tissue paper sheets

[0044] The paper sheets produced for the reference formulations **REF 1** and **REF 2** and with fibres of unbleached *Eucalyptus globulus* pulp **UBP 1**, **UBP 2**, **UBP 3** and **UBP 4** were analyzed and major results are depicted in Table 6.

Table 6. Results obtained for the properties of paper sheets of 20 g/m^2 with unbleached *Eucalyptus globulus* pulp, unrefined (formulation = %**SF**:%**LF**:%**UBP**).

	REF1 (70:30:0)	REF2 (100:0:0)	UBP1 (35:30:35)	UBP2 (20:30:50)	UBP3 (0:30:70)	UBP4 (0:0:100)
Weight, g/m^2	21.1±0.3	21.1±0.4	21.3±0.2	21.3±0.6	21.7±0.3	21.4±0.2
Thickness, μm	135.4±7.02	127.3±5.55	137.9±4.23	145.0±6.58	150.7±4.45	143.7±3.16
Bulk, cm^3/g	6.42±0.36	6.04±0.32	6.48±0.23	6.77±0.18	6.94±0.25	6.72±0.13
Tensile index, Nm/g	4.44±0.32	4.42±0.26	6.66±0.2	8.12±0.29	9.45±0.42	9.47±0.16
Absorption capacity, g_{H2O}/g_{paper}	8.05±0.04	7.54±0.26	8.74±0.14	9.47±0.04	9.63±0.12	9.26±0.15
Air permeability , L/m^2/s	804±85	741±86	1012±59	1063±83	1093±61	1055±35
Softness, HF	80.5±1.9	80.5±2.5	77.8±2.3	78.3±1.5	74.8±4.2	77.7±1.7
Softness,TS 7	13.0±1.0	13.4±1.35	14.5±1.22	14.0±0.8	15.7±2.25	14.3±0.89
Softness,TS 750	13.3±1.3	11.6±0.4	13.3±0.7	13.1±1.2	15.0±3.5	13.1±0.8
Klemm Capillarity, mm						
10 s	27.5±3.5	25.0±2.8	28.8±0.4	25.8±1.5	23.0±1.4	20.8±4.3
20 s	38.5±2.7	33.8±1.1	38.0±1.2	37.3±1.9	31.5±1.5	27.5±3.2
30 s	45.8±1.3	40.8±2.5	45.8±0.8	42.8±0.8	39.3±2.2	34.3±2.2
60 s	59.5±1.5	54.8±3.4	60.3±1.1	57.8±1.8	54.0±1.9	46.8±1.5
180 s	91.3±1.1	87.0±4.1	94.0±1.0	91.5±2.7	83.0±3.1	77.8±1.5
300 s	112.0±0.7	105.3±5.4	115.0±2.5	110.3±3.1	103.0±7.0	94.5±1.1

[0045] The results show that with the incorporation of unbleached *Eucalyptus globulus* pulp (**UBP**) a bulk increase is

obtained compared to **REF 1** and **REF 2**. In addition, the increase of the **UBP** content also led to a significant increase in the tensile index, with **UBP 3** and **UBP 4** showing an up to 115% increase compared to **REF 1.**

[0046] Concerning air permeability, the increase in **UBP** resulted in a higher permeability compared to the references, which suggests a more porous structure.

[0047] In terms of capillarity, there is a slight decrease in the capillary rise with the incorporation of **UBP** fibers.

[0048] For the absorption capacity a higher incorporation of **UBP** led to an improvement of the water absorption capacity.

[0049] The presented softness results, with the incorporation of *Eucalyptus globulus* unbleached pulp, revealed a very slight softness variation (within the measurement error) comparing to the references.

ii. Paper properties - 60 g/m^2 tissue papers sheets

[0050] 60 g/m^2 paper sheets produced through the formulations with unrefined **UBP** incorporation were analyzed and the results are shown in Table 7.

Table 7. Results obtained for the properties of paper sheets of 60 g/m^2 with unbleached *Eucalyptus globulus* pulp, unrefined (formulation= %**SF :** %**LF :** %**UBP**).

	REF1 (70:30:0)	REF2 (100:0:0)	UBP1 (35:30:35)	UBP2 (20:30:50)	UBP3 (0:30:70)	UBP4 (0:0:100)
Weight, g/m^2	64.5±0.02	64.7±0.01	64.7±0.02	63.0±0.03	64.2±0.02	64.8±0.01
Thickness, μm	97.8±7.9	113.9±13.4	109.6±7.5	109.3±8.4	107.8±2.3	103.8±3.7
Bulk, cm^3/g	1.25±0.06	1.76±0.08	1.69±0.08	1.63±0.08	1.68±0.08	1.60±0.08
Tensile index, Nm/g	19.0±0.2	21.0±1.6	26.5±1.6	29.5±3.1	33.5±3.1	40.0±3.1
Tear index, mN.m^2/g	6.4±0.7	3.1±0.71	8.5±0.8	8.2±1.1	9.7±0.5	6.27±0.7
Burst index, kPa.m^2/g	1.30±0.09	0.95±0.12	1.51±0.13	1.83±0.12	2.01±0.06	2.42±0.17
Extension, %	1.2±0.1	1.1±0.2	1.7±0.3	1.7±0.5	2.2±0.3	2.2±0.4
Opacity, %	76.9±0.5	78.6±0.4	91.7±0.4	95.1±2.2	94.7±0.8	96.7±0.8
Gurley air resistance, s	3.6±0.3	0.90±0.11	1.0±0.07	1.0±0.05	1.1±0.09	1.0±0.14
Scott Test, J/m^2	326±40	103±8	141±10	170±9	171±16	228±15
Capillarity , mm/10min	61.0±2.0	92.0±3.0	78.0±3.0	74.0±3.0	73.0±2.9	61.0±4.1

[0051] The obtained results are in agreement with the studies for the paper sheets of 20g/m^2.

[0052] The replacement of short fiber by **UBP** also allowed obtaining higher values of tensile, tear and burst indexes values than the references (**REF 1** and **REF 2**). Scott Test results values showed a decrease with the incorporation of **UBP** in comparison with **REF 1** (70:30:0) but, on the other hand, an increase over **REF 2** (100:0:0).

c. Refined pulps

i. Paper properties - 20 g/m^2 tissue paper sheets

[0053] Paper sheets were produced with the refined pulps with a °SR of 25, considering the reference formulations **REF 1** and **REF 2** and with unbleached *Eucalyptus Globulus* kraft pulp fibers **UBP 1**, **UBP 2**, **UBP 3** and **UBP 4**. The main results from the analysis of their paper properties are shown in Table 8.

Table 8. Results obtained for the properties of paper sheets of 20 g/m^2 with unbleached Eucalyptus globulus pulp, refined to a 25 °SR (formulation= %**SF** : %**LF** : %**UBP**).

	REF1 (70:30:0)	REF2 (100:0:0)	UBP1 (35:30:35)	UBP2 (20:30:50)	UBP3 (0:30:70)	UBP4 (0:0:100)
Weight, g/m^2	21.2±0.3	21.3±0.4	21.1±0.2	21.5±0.5	21.7±0.4	21.4±0.3
Thickness, μm	101±2.8	109.9±2.9	100.3±2.1	114.1±3.2	114.2±2.8	129.3±3.5
Bulk, cm^3/g	4.30± 0.17	5.15±0.16	4.29±0.12	4.78±0.20	4.74±0.13	6.04±0.19
Tensile index, Nm/g	29.3±0.73	23.3±0.73	30.4±0.43	28.9±0.71	29.6±0.7	22.5±0.29
Absorption capacity, g_{H2O}/g_{paper}	7.0±0.3	7.4±0.2	6.7±0.1	7.2±0.3	7.6±0.1	8.3±0.2
Air permeability, L/m^2/s	446±18	568±27	499±36	578±37	623±37	703±182
Softness, HF	54.2±4.8	63.7±4.7	53.8±5.5	57.3±4.9	63.8±5.8	68.8±1.5
Softness, TS7	28.9±2.4	22.7±5.6	28.2±2.9	26.0±2.64	22.5±3.11	19.5±0.8
Softness, TS750	23.7±3.6	21.0±3.2	24.0±3.2	23.2±1.6	23.8±2.1	19.1±3.2
Klemm Capillarity, mm						
10 s	23.3±2.3	24.5±0.5	20.3±1.9	23.8±1.1	19.3±2.5	20.0±1.0
20 s	32.0±2.1	32.5±1.1	26.3±4.2	30.8±0.4	27.0±2.1	28.5±0.5
30 s	37.8±1.8	39.0±1.2	32.3±2.5	37.5±0.5	32.3±1.3	34.0±1.0
60 s	51.0±2.4	51.8±1.8	43.5±2.7	52.0±1.0	43.3±1.3	42.0±1.0
180 s	80.3±2.5	82.5±8.9	71.0±4.3	81.8±1.9	68.3±1.5	73.5±1.5
300 s	98.8±4.8	102.0±3.3	87.3±5.5	99.8±2.2	85.3±1.9	88.5±3.5

[0054] Analyzing the paper properties of the paper sheets produced with the refined pulps, it was found that, even with refining, the bulk increases with the incorporation of refined **UBP**. Additionally, and as previously noted, the absorption capacity also increases with the incorporation of refined **UBP**. Regarding the tensile index, there was also an increase for **UBP 1** and **UBP 3**, compared to **REF 1**.

[0055] For softness there is an increase with the incorporation of refined **UBP**, when comparing to the reference samples, particularly **REF 1** (up to 9.6 HF points).

ii. Paper properties - 60 g/m^2 tissue paper sheets

[0056] 60 g/m^2 paper sheets were produced with 25°SR refined pulps and the main results of the analysis of their paper properties are shown in Table 9.

Table 9. Results obtained for the properties of paper sheets of 60 g/m^2 with unbleached Eucalyptus globulus pulp, refined to a 25 °SR (formulation= %**SF** : %**LF** : %**UBP**).

	REF 1 (70:30:0)	REF 2 (100:0:0)	UBP 1 (35:30:35)	UBP 2 (20:30:50)	UBP 3 (0:30:70)	UBP 4 (0:0:100)
Weight, g/m^2	64.9±0.02	64.8±0.01	64.2±0.03	64.4±0.02	65.0±0.02	67.4±0.01
Thickness, μm	95.8±3.2	102.9±3.60	95.0±1.40	95.5±4.30	98.1±2.80	104.6±7.30
Bulk, cm^3/g	1.48±0.02	1.59±0.02	1.48±0.04	1.48±0.02	1.51±0.03	1.55±0.01

(continued)

	REF 1 (70:30:0)	REF 2 (100:0:0)	UBP 1 (35:30:35)	UBP 2 (20:30:50)	UBP 3 (0:30:70)	UBP 4 (0:0:100)
Tensile index, Nm/g	52.5±1.7	42.5±1.7	56.5±3.41	57.0±1.94	58.5±1.88	49.5±2.23
Tear index, $mN.m^2/g$	9.5±0.5	6.4±0.60	9.6±0.49	9.8±0.50	10.2±0.50	7.2±0.43
Burst index, $kPa.m^2/g$	3.4±0.2	2.2±0.2	3.6±0.2	3.6±0.2	3.9±0.1	2.8±0.2
Extension, %	2.9±0.1	2.3±0.1	3.0±0.2	2.8±0.2	3.0±0.2	2.5±0.1
Opacity, %	72.2±0.76	75.6±0.35	89.1±0.7	91.4±0.71	93.8±0.35	96.4±0.8
Gurley air resistance, s	4.0±0.26	1.90±0.13	3.7±0.18	3.8±0.22	3.4±0.26	2.1±0.24
Scott Test, J/m^2	210±15	187±12	234±29	243±21	249±22	209±19
Capillarity , mm/10min	64.0±1.3	82.0±2.99	60.0±3.0	48.0±2.2	59.0±1.4	71.0±2.2

[0057] Analyzing the results from Figure 10, it can be seen that the incorporation of refined UBP led to an increase in the tensile index, tear, opacity, in the Scott test results (internal bonding) and an increase in bulk.

[0058] Regarding capillarity, with the incorporation of refined **UBP** the values of this parameter decreased.

[0059] The incorporation of unbleached pulp, refined or not, allows an increased bulk, increased physical and mechanical properties and increased absorption capacity. In terms of softness, there is an increase of this property up to 9.6 HF points with refined pulp. Based on the results obtained, it can be concluded that replacing bleached pulp with semi-bleached or unbleached *Eucalyptus globulus* pulp has a numerous of advantages.

[0060] In terms of key tissue properties, the use of semi-bleached or unbleached *Eucalyptus globulus* pulp enables the development of consumer-appreciated properties such as bulk, strength, absorption, softness and even visual perception, the later which can be coupled with sustainability and environmental concerns.

[0061] In addition, being semi-bleached or unbleached pulp, less chemicals (bleaching agents are less or no longer needed) and less water (bleaching process is a step where a significant water consumption is observed) are used for its production.

[0062] Based on this, reducing the consumption of chemicals and water not only makes the pulp production process more environmentally friendly, but it also allows savings in raw materials production costs (lower water and reagent consumption).

Claims

1. A pulp for tissue products production comprising semi-bleached or unbleached *Eucalyptus globulus* fibers.

2. The pulp according to claim 1, having a viscosity of not less than 1300 mL/g and a carboxyl content of not less than 10%, and comprising fibers having a length of not less than 0.8 mm, a width of not less than 19 μm and a coarseness of not less than 6 mg/100m.

3. Use of the pulp described in any of the claims 1 and 2 for the production of tissue products.

4. Tissue paper sheets comprising the pulp described in any of the claims 1 and 2.

5. The tissue paper sheets according to claim 4, comprising a minimum of 35% (w/w) of the pulp described in any of the claims 1 and 2.

6. The tissue paper sheets according to any of the claims 4 and 5, having a bulk greater than 1 cm^3/g, a tensile index greater than 4 kN.m/kg, an absorption capacity greater than 7 gH_2O/g_{paper}, an air permeability greater than 450

$L/m^2/s$ and a softness greater than 50 HF.

7. The tissue paper sheets according to any of the claims 4 to 6, having a bulk from 2 to 7 cm^3/g, a tensile index from 6 to 60 kN.m/kg, an absorption capacity from 7 to 10 gH_2O/g_{paper}, an air permeability from 500 to 1090 $L/m^2/s$ and a softness from 55 to 80 HF.

8. The tissue paper sheets according to any of the claims 4 to 7, having a tear index greater than 6 $mN.m^2/g$, a burst index greater than 1 $kPa.m^2/g$, a capillarity of not less than 60 mm/10min and an opacity greater than 70 %.

9. The tissue paper sheets according to any of the claims 4 to 8, having a tear index from 6 to 10 $mN.m^2/g$, a burst index from 1 to 4 $kPa.m^2/g$ and an opacity greater than 90 %.

10. Use of the tissue paper sheets described in any of the claims 4 to 9 for the production of household and sanitary products.

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EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	16 June 2020	Karlsson, Lennart

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Munich	16 June 2020	Karlsson, Lennart

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