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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 October 2017 (19.10.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/178849 A1

(51) International Patent Classification:
D21C 3/02 (2006.01) *D21C 11/00* (2006.01)
D21C 9/10 (2006.01) *D21H 11/12* (2006.01)
D21C 9/16 (2006.01)

(21) International Application Number:
PCT/HR2016/000014

(22) International Filing Date:
15 April 2016 (15.04.2016)

(25) Filing Language: English

(26) Publication Language: English

(72) Inventor; and
(71) Applicant : MIKULIC, Marinko [HR/HR]; Luksic Gornji 7, HR-10000 Zagreb (HR).

(74) Agent: BIHAR, Zeljko; Admoveo d.o.o., Aleja lipa 1/G, HR-10040 Zagreb (HR).

(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, 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, ST, 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).

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

(54) **Title**: A CONTINUOUS PROCESS FOR PRODUCTION OF CELLULOSE PULP

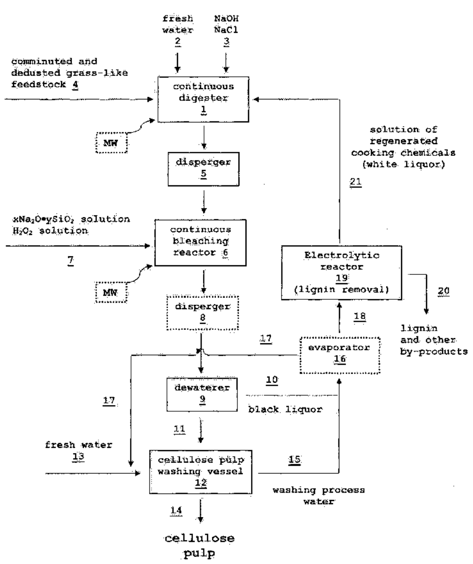


Figure 1

(57) Abstract: The present invention discloses the continuous process for production of cellulose pulp of very high whiteness from grass-like plant feedstock suitable for paper making. Process comprising the steps of: preparing the grass-like plant feedstock by comminuting; dedusting; continuous digestion with optimized concentrations of NaOH and NaCl; disperging; continuous bleaching with optimized concentrations of H_2O_2 and sodium silicate without the use of NaOH; optional disperging; dewatering to remove the black liquor; and washing, to yield final cellulose pulp of very high whiteness, >90%, suitable for manufacturing of paper or cellulose sheets. The process additionally includes integrated electrolytic removal of lignin and other by-products accompanied with regeneration of cooking chemicals solution, what enables completely closed process materials cycle. In one form of invention, heating of digesting and bleaching steps can be optionally performed by microwave (MW) heating. The preferred grass-like feedstock for the process is miscanthus (*Miscanthus x giganteus*, Andersson).

WO 2017/178849 A1

A CONTINUOUS PROCESS FOR PRODUCTION OF CELLULOSE PULP

DESCRIPTION

Technical Field

The invention is related to an improved continuous process for production of cellulose pulp of very high whiteness, >90%, and lignin content <5% w/w, from comminuted grass-like feedstock such as miscanthus (*Miscanthus x giganteus*, Andersson).

Technical Problem

The main technical problem, solved by the present invention, is formation of the novel process for production of cellulose pulp having high whiteness, from a grass-like feedstock in an effective way. This effective way is achieved by using as little as possible of inexpensive environmentally-acceptable chemicals and under as mild as possible digestion and bleaching conditions. Also, such process should ensure maximal preservation of natural cellulose fibers from the starting feedstock.

Conventional cellulose pulp manufacturing uses sulphur-based chemicals with high water and energy consumption or milder sodium hydroxide based processes but with high energy consumption on intensive pulp disperging, what all together have a great overall negative impact on the environment.

Most important features of any successful pulp production from grass-like feedstock are to ensure:

(i) as mild as possible digestion of comminuted plant material to remove unwanted non-cellulosic fraction, predominantly lignin;

(ii) using minimal mechanic share force including mild disperging and further processing of a pulp suspension;

(iii) careful and effective bleaching; in order to preserve natural cellulose fibers what is the key base for high quality paper;

(iv) effective removal of lignin and other non-cellulosic by-products up to acceptable level, preferably to <5% w/w; and with

(v) efficient regeneration of digesting chemicals and processing water from the black liquor to ensure closed-cycle of process material balance and thus minimal environmental impact.

The first technical problem solved with the disclosed invention is to use milder and optimized chemical reagents during digestion and bleaching steps and very high whiteness, higher than 90%, thus avoiding harsh and high energy-consuming manufacturing conditions, dangerous and sulphur-based chemicals, and environment pollution with waste waters containing residues of all these processing chemicals.

The technical problem solved with the disclosed invention is to find a solution within the frame of "green"-chemical technology, characterized by:

(a) very mild digestion and bleaching conditions with a novel hydrogen peroxide (H_2O_2)-based bleaching system without the use of sodium hydroxide;

(b) high concentration of cellulose suspension during digestion; thus high cellulose output per volume (productivity);

(c) high preservation of natural fibers from the feedstock by using mild digesting and bleaching reactions conditions, as well as minimal mechanical stress during disperging and optional screening; and

(d) complete regeneration of digesting chemicals and process waters practically without affecting the environment, in integrated manner, so that removal of lignin and other non-cellulosic by-products from spent (black) liquor and waste water is accompanied with regeneration of digesting chemicals solution - so called a "white liquor".

According to our best knowledge, this is the first eco-friendly process for cellulose pulp manufacturing that operates at such mild digestion conditions, with very low water consumption, low energy consumption, which can produce cellulose of very high whiteness, higher than 90%, with <5% w/w of lignin, which can yield top-quality paper of excellent mechanical properties. The process according to this invention does operate well only when grass-like feedstock is employed.

Previous State of the Art

Production of cellulose pulp for paper manufacturing from renewable, fast-growing, and more economic plant feedstock is of an increasing importance in modern paper industry. In this manner, classical wood-based processes are becoming to be replaced with grass-like feedstock like miscanthus (*Miscanthus x giganteus*, Andersson), switchgrass (*Panicum virgatum*, Linne), sorghum (*Sorghum* species, Linne), common reed (*Phragmites australis*, Cav.), giant reed (*Arundo donax*, Linne), straw of various cereals, etc.

For instance, miscanthus (*Miscanthus x giganteus*, Andersson) is one of most suitable grass-like feedstock for such use; see references 1 and 2:

1) G. Wegener: Pulping innovations in Germany, *Ind. Crops Prod.* **1** (1992) 113-117;
2) C. Cappelletto, F. Mongardini, B. Barberi, M. Sannibale, M. Brizzi, V. Pignatelli: Papermaking pulps from the fibrous fraction of *Miscanthus x Giganteus*, *Ind. Crops Prod.* **11** (2000) 205-210.

Within the pulp manufacturing process, the most important phase is digestion. This means the cooking of comminuted lignocellulosic material in the aqueous solution of suitable digestion chemicals. There exist several pulping processes regarding the chemicals used. The most known technologies are based on digestion with solutions of:

(i) sulphur-containing chemicals: sodium carbonate (Na_2CO_3) and sodium sulfite (Na_2SO_3), magnesium hydroxide [$Mg(OH)_2$] and magnesium sulfite ($MgSO_3$), ammonium hydroxide (NH_4OH) and ammonium sulfite [$(NH_4)_2SO_3$], calcium hydrogensulfite [$Ca(HSO_3)_2$], magnesium hydrogensulfite [$Mg(HSO_3)_2$], sodium hydroxide (NaOH), sodium sulphide (Na_2S) and sodium sulphate (Na_2SO_4);

(ii) non-sulphur containing chemicals: sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH); and

(iii) acids like nitric acid (HNO_3).

Such solution of digesting chemicals is also known as „white liquor", representing either fresh or regenerated solution of digestion chemicals. The white liquor helps to remove non-cellulosic materials, which are thus dissolved in the solution, leaving relatively pure cellulose fibers suspended in this liquid phase.

Cooked feedstock with removed non-cellulosic materials, i.e. a „pulp", is, at the end of digestion, suspended in used solution, which contains various chemical forms of non-cellulosic plant ingredients and remains of digestion chemicals. This aqueous phase is called the „black liquor". Thus, the pulp after the digestion is a suspension of essentially pure cellulose fibers in the black liquor.

Regarding the type of digestion, as one of the most important technological aspect of the pulp manufacturing, processes which are based on diminished use of sulphur-based chemicals are of significant advantages. The most prominent reason is ecology. The use of sulphur-free processes are of top importance in preserving environment, also avoiding corrosion problems at production equipment, as well as toxicology issues.

One of the most environmentally-friendly sulphur-free processes uses sodium hydroxide-based technology. The use of sodium hydroxide (NaOH) as sole digesting chemical is known in the art and also specifically in the processed based on grass-like feedstock such as rice straw, esparto, reed, jute, and others. One of the processes is performed with 5% aqueous solution of sodium hydroxide (NaOH) at 90 °C for several hours; see reference 3:

3) GB 770,687; Method of producing cellulose; applicant Aschaffenburger Zellstoffwerke (DE).

The digestion steps can be performed with microwave (MW) assisted heating. Thus Zhu and co-workers described the pretreatment process of miscanthus /*Miscanthus x giganteus*, Andersson/ with sodium hydroxide (NaOH) solution at very high temperatures (130-200 °C) at elevated pressures during 20 minutes under MW heating. Such pre-treated miscanthus further gave much better yield in sulphuric acid (H_2SO_4)-catalysed hydrolysis to glucose as a feedstock to fermentation into bioethanol; see reference 4:

4) Z. Zhu, D. J. Macquarrie, R. Simister, L. D. Gomez, S. J. McQueen-Mason: Microwave assisted chemical pretreatment of Miscanthus under different temperature regimes, *Sustain. Chem. Process* **3** (2015) DOI: 10.1186/s40508-015-0041-6.

Although this process is focused on production of glucose from miscanthus, such pre-treatment suggests some potential in the use of MW for miscanthus digestion. Of course, the reaction conditions disclosed in the reference 4 are very harsh and clearly not compatible with production of high quality cellulose fibers with high whiteness.

Beside digestion, the bleaching is another important key step in manufacturing of cellulose of high whiteness is the bleaching step. The most common systems for cellulose bleaching are those based on chlorine-containing systems, e.g. sodium hypochlorite (NaOCl), or hydrogen peroxide (H_2O_2)-based systems, the latter one being preferred.

Thus the patent GB681661 discloses a process for bleaching cellulose pulp by the use of the following bleaching system:

(a) 0.30-1.75% hydrogen peroxide (H_2O_2);

(b) 0.75-3.25% sodium hydroxide (NaOH);

(c) 20-65% cellulose pulp (dry matter); and

(d) ad 100% process water;

at temperatures below 54.4 °C (130 °F). Optionally, sodium silicate ($xNa_2O \bullet ySiO_2$) solution is used as a hydrogen peroxide-stabilizer; see reference 5:

5) GB681661A; Treatment of Chemical Pulp; applicant: Buffalo Electro-Chemical Co., Inc. (US).

This document suggests the use of a combination of hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH) as the bleaching system for cellulosic materials at relatively mild reaction conditions, below 54.4 °C. The use of sodium silicate solution is mentioned only in the context of its stabilizing action on H_2O_2.

The present invention is also based on hydrogen peroxide (H_2O_2)-bleaching, but the main, crucial, and advantageous difference is in the use of a combination of H_2O_2 and sodium silicate solution ($xNa_2O \bullet ySiO_2$), essentially without the use of sodium hydroxide (NaOH) as a co-reagent which, in reaction with H_2O_2, generates equilibrium concentration of hydroperoxide anions (HOO^-) as actual oxidizing species.

Beside conventional heating in the cellulose pulp bleaching process, microwave (MW)-assisted heating has also been employed. In this manner, Law disclosed the method and apparatus for MW-assisted bleaching of cellulose pulp; see reference 6:

6) CA2038651A1; K.-N. Law: Method and apparatus for bleaching pulps; applicants: K.-N. Law, J. L. Valade (US).

Moreover, Law and co-workers described the method for cellulose pulp bleaching by the use of MW-heating and a combination of bleaching chemicals consisting of hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH). In this process, sodium silicate solution can also be optionally employed as the stabilizer for H_2O_2; see reference 7:

7) K. N. Law, S. G. Luo, J. L. Valade: Characteristics of Peroxide Bleaching of Microwave-Heated Thermomechanical Pulps, *J. Pulp Paper Sci.* **19** (1993) J181-J-186.

Both documents teach that MW, in general, can be used as alternative heating means in the cellulose pulp bleaching processes. However, these documents remain silent about the effect of combined hydrogen peroxide (H_2O_2) - sodium silicate ($xNa_2O{\bullet}ySiO_2$) system, without the use of highly alkaline sodium hydroxide (NaOH), on efficacy (yield, quality and whiteness) of cellulose pulp bleaching from grass-like feedstock.

Additionally, one feature of the process for manufacturing of cellulose pulp of very high whiteness is certainly whether the cooking chemicals from the digestion phase is removed from the pulp or they can be retained in the pulp before the bleaching step.

The older processes performed removal of the black liquor which contains digesting chemicals, lignin, and other non-cellulosic by-products.

Abu and co-workers disclosed a process for production of fibrous cellulose material which includes: (1) comminuting of plant material, (2) mixing it with 0.5-1% aqueous sodium hydroxide (NaOH) solution, (3) sieving, (4) passing thus obtained material from extruder wherein the material is mixed with hydrogen peroxide (H_2O_2)

at 120-150 °C at 20 bar, and (5) discharging out from the extruder and washing with water; see reference 8:

8) DE19603491A1; Production of fibrous cellulose material free from other plant components; applicants: S. I. Abu, D. Kistmacher, R. Berg (DE).

This document suggests the possibility of continuous processing of cellulose-containing plant material with digesting chemicals such as sodium hydroxide (NaOH) and further bleaching with hydrogen peroxide (H_2O_2), without the use of intermediary washing out of digestion chemicals (NaOH) before the bleaching.

The present invention is also characterized by one of key details that it does not involve washing out of remaining cooking chemicals after digestion phase, but directly undergoes to disperging and bleaching steps.

However, the key difference between the process from the present invention and DE19603491A1 is in the facts that the former process uses:

(i) digestion system based on specific, optimized concentrations of digesting chemicals NaOH and NaCl; and
(ii) bleaching system based on also specific and optimized concentrations of H_2O_2 and sodium silicate, essentially without any additional NaOH.

Mikulic disclosed a continuous process for production of cellulose pulp from grass-like feedstock such as miscanthus (*Miscanthus x giganteus*, Andersson), using a vertical digester with smooth internal walls without any screen or mixing element inside, by the use of very dilute cooking chemicals, sodium hydroxide (NaOH) and sodium chloride (NaCl) or sodium sulphite (Na_2SO_3), with the following average composition of digesting suspension:

(a) 0.90-1.50% w/w of NaOH;
(b) 0.15-0.40% w/w of NaCl or Na_2SO_3;

(c) 15-18% w/w of comminuted grass-like feedstock; and

(d) ad 100% of process water;

wherein the digesting process is heated by conventional means, either through direct heating of the digester or with heating medium; see reference 9.

Beside a new type of simplified vertical digester, this process is also based on subsequent processing of cooked pulp within the screening and fractionation device which isolate a good cellulose pulp fraction and separate the improper one. The later is further subjected to pulp milling in one or more suitable pulp mills yielding the proper cellulose pulp. This can be further optionally bleached with conventional bleaching chemicals to yield high quality cellulose suitable for paper production.

According to our best knowledge, this is the closest prior art document for the present invetion; see reference 9:

9) WO2015/150841A1; M. Mikulic: A Continuous Process for Production of Cellulose Pulp from Grass-like Feedstock; applicant: M. Mikulic.

In contrast to document WO2015/150841A1, the process from the present invention employs a combination of:

(a) specific and optimized concentration of digesting chemicals, sodium hydroxide (NaOH) and sodium chloride (NaCl), and at a lower content of feedstock in the digesting suspension, 10-15% w/w of dry matter;

(b) disperging; essentially without removal of remained cooking chemicals, subsequent,

(c) modified bleaching process based on specific and optimized concentrations hydrogen peroxide (0.50-2.00% w/w H_2O_2) and sodium silicate (0.50-2.00% w/w $xNa_2O\bullet ySiO_2$) solutions, essentially without additional sodium hydroxide (NaOH) use for bleaching purpose; as well as

(d) integrated electrolytic regeneration of cooking chemicals and isolation of lignin and other by-products, what enables high effective cellulose manufacturing with fully closed cycle of the process materials.

The digestion (a) and bleaching (c) processes can be performed by microwave (MW)-assisted heating with comparable good results within significantly shorter period of time for each step.

The combination of steps (a)-(c) results in very high quality cellulose pulp of very high whiteness, >90%, with <5% w/w of lignin, which cannot be produced by the process disclosed in the reference 9.

The removal of lignin and other by-products from the black liquor solution by the use of electrolytic reactor (cell) is known in the art. Typical example of such technology was disclosed by Edel and co-workers; see reference 10:

10) US4584076A; E. Edel, J. Feckl, C. Grambov, A. Huber, D. Wabner: Process for obtaining lignin from alkaline solutions thereof; applicant: MD Organocell Zellst Umwelttec (DE).

Briefly, during electrolysis of the black liquor solution by the use of direct current (DC) within suitable electrodes, lignin and other by-products are separated in the anode compartment, whilst the regeneration of sodium hydroxide (cooking solution or white liquor) is regenerated in the cathode compartment.

The process from this invention uses roughly similar electrolytic reactor for removal of lignin and other by-products and for parallel regeneration of cooking chemicals, NaOH + NaCl solution (white liquor), but the main and crucial difference is in the fact that the electrolytic process in this invention works with the black liquor solution comprising dilute sodium lignin and sodium chloride (NaCl). In this manner, the black liquor solution from this invention is of better conductance due to sodium chloride presence, whilst the process from reference 10 is based on processing sole sodium lignin from Organosolv technology for cellulose manufacturing.

The process from the present invention provides very high quality cellulose of very high whiteness, >90%, at high yield, at very low water and energy consumption.

The technology for production of cellulose pulp from grass-like feedstock according to this invention represents a novel and inventive technology, as is disclosed in the detailed description of the invention.

Summary of the Invention

The present invention discloses a continuous process for production of cellulose pulp of very high whiteness from grass-like plant feedstock. The process comprising the steps of:

(i) preparing the grass-like plant feedstock by comminuting to produce a feedstock with longitudinal size distributed from 5-30 mm and diameter of 0.1-2 mm, and with removed fine dusty particles by dedusting of said feedstock with fan;

(ii) continuous digestion of a grass-like dust-free plant feedstock prepared in step (i) in a continuous digester (1) formed as a longitudinal column internally equipped with worm screw conveyor and a heating unit; where grass-like plant feedstock is continuously fed directly on the top of the said digester via conveyor (4);

where in parallel with said feedstock feeding, the chemicals for digestion, sodium hydroxide (NaOH) and sodium chloride (NaCl), and fresh water and/or regenerated white liquor, are introduced continuously on the top of said digester (1); maintaining the digestion temperature from 70-120 °C and average composition of thus formed suspension during said continuous digestion is keeping within the following ranges:

(a) 0.50-2.00% w/w of NaOH;

(b) 0.50-1.50% w/w of NaCl;

(c) 10-15% w/w of grass-like plant feedstock; and

(d) process water; up to 100% w/w of the suspension;

wherein the weight percentages of ingredients being calculated on the weight of the whole suspension;

where a dissolution of non-cellulosic substances from the grass-like plant feedstock occurs during the mass transfer from one to the other side of the said longitudinal digester that lasts 1.5-3 hours;

(iii) where cooked pulp is continuously, by equal rate as being feedstock fed into the digester (1), discharged from the said digester (1), via conveyor, directly into disperger (5), where the suspended cellulose pulp is subjected to main disperging, yielding finely disperged cellulose fibers;

(iv) where thus obtained fine suspension of disperged cellulose pulp is further subjected to bleaching:

(a) without any removal of chemicals from the digestion phase (ii); and

(b) without the use of any additional NaOH for the bleaching purpose; and

where disperged cellulose pulp is continuously fed into the continuous bleaching reactor (6) which is, analogously to the digester (1), formed as a longitudinal column internally equipped with worm screw conveyor and a heating unit;

where bleaching chemicals selected from the group comprising:

(a) 20-40% w/w aqueous hydrogen peroxide (H_2O_2) solution; and

(b) 30-45% aqueous sodium silicate ($xNa_2O{\bullet}ySiO_2$) solution with the molar ratio $Na_2O:SiO_2$ = 1:1 to 3.3:1; which

are introduced through manifold (7) into the bleaching reactor (6), maintaining the bleaching temperature from 70-100 °C, during 45 minutes to 1.5 h, and average composition of thus formed suspension during whole bleaching process is keeping within the following ranges:

(a) 0.50-2.00% w/w of said H_2O_2 solution;

(b) 0.50-2.00% w/w of said $xNa_2O{\bullet}ySiO_2$ solution;

(c) 10-15% w/w of cellulose; and

(d) process water; up to 100% w/w of the suspension;

wherein the weight percentages of ingredients being calculated on the weight of the whole suspension;

(v) the suspension of thus obtained bleached cellulose pulp, discharged from the bleaching step (iv), is optionally further processed through the disperger (8); and then transferred into the dewaterer (9);

(vi) where the bleached and eventually additionally disperged cellulose pulp is dewatered, separated from the black liquor yielding:

(a) bleached cellulose pulp of 10-15% w/w dry matter; and

(b) the black liquor containing lignin and other cooking and bleaching by-products; and

(vii) the bleached cellulose pulp is additionally washed in the washing vessel (12) with additional fresh water, which is introduced through the manifold (13), giving:

(a) final bleached and washed cellulose pulp, of very high whiteness, higher than 90%, of 10% w/w dry matter, and lignin content >5% w/w, which is transported out from the whole process through manifold (14); and

(b) additional amount of washing process water, which is transferred via manifold (15), together with the black liquor from the dewatering step (vi), which is transported via manifold (10), into the electrolytic reactor (19);

(viii) where the black liquor and washing process water are subjected to electrolysis with direct electric current (DC) between two electrodes, at electric potential of 3-30 V, and electric current density of 1-10 A/dm^2, at 10-95 °C, wherein the lignin and by-products are separated on the top of the electrolyte solution in the anode compartment, and continuously removed from the electrolytic reactor; and

wherein the resulting electrolyte solution with regenerated NaOH and NaCl solution, representing the white liquor, is regenerated from the cathode compartment back to the cooking process, via manifold (21), to the continuous digester (1), thus closing the whole cellulose-manufacturing process.

The continuous process for production of cellulose pulp according to the present invention optionally further involves the following manufacturing steps:

(ix) screening and fractionation, where diluted suspension from the step (vii) is processed through a screening and fractionation device (22) equipped with 0.1-0.5 mm sieve, yielding two fractions;
 (a) the first fraction that does not pass through the 0.1-0.5 mm screen; and
 (b) the second fraction that passes through the 0.1-0.5 mm screen, which is considered as a good cellulose pulp of very high whiteness, higher than 90%, suitable for manufacturing of top-quality paper or cellulose sheets, which is transported out from the whole process through manifold (23); and

(x) cellulose pulp milling; where the (a) fraction of the cellulose pulp from the step (ix), is subjected to one or two subsequent processing through the pulp mills (24,25) yielding the cellulose pulp, which is transferred, via manifold (26), to the screening and fractionation device (22).

In another embodiment of this invention, the cooking chemicals for the digestion step (ii) are introduced as a mixture of concentrated aqueous solutions of 20-50% w/w NaOH and 10-30% w/w of NaCl.

The continuous digestion phase (ii) is preferably carried out at 90-100 °C.

Additionally, in other embodiment of the present invention, the bleaching chemicals for the bleaching step (iii) are introduced to the continuous bleaching reactor (6) in the form of concentrated aqueous solutions of 30-45% w/w sodium silicate ($xNa_2O \bullet ySiO_2$); and 20-40% w/w of hydrogen peroxide (H_2O_2).

The continuous bleaching process is preferably performed at 85-100 °C.

The continuous process for production of cellulose pulp according to the present invention can be alternatively carried out by the use of microwave (MW)-assisted heating. In this case, the heating units in the continuous digester (1) and/or continuous bleaching reactor (6) are microwave (MW)-generating magnetrons.

The grass-like feedstock that can be processed by the process of this invention includes the stems of plant species selected from the group of: wheat (*Triticum* vulgare, Linne); rice (*Oryza* sativa, Linne); barley (*Horedum vulgare*, Linne); oat (*Avena sativa*, Linne); flax (*Linum usitatissimum*, Linne); maize (*Zea mays*, Linne); millets: proso millet (*Panicum miliaceum*, Linne), pearl millet (*Pennisetum glaucum*, Linne), browntop millet (*Panicum ramosum*, Linne), and barnyard (*Echinochloa frumentaceae*, Linne); triticale (x *Triticosecale*, Wittm. ex A. Camus); buckwheat (*Fagopyrum esculentum*, Moench); miscanthus (*Miscanthus x giganteus*, Andersson); switchgrass (*Panicum virgatum*, Linne); sorghum (*Sorghum* species, Linne); common reed (*Phragmites australis*, Cav.), giant reed (*Arundo donax*, Linne), burma reed (*Neyraudia reynaudiana*, Kunth.), reed-mace (*Typha* spp., Linne), paper reed (*Cyperus papyrus*, Linne), bur-reed (*Sparganium* spp., Linne), thatching reed (*Thamnochortus insignis*, Linne); esparto grass (*Stipa tenacissima*, Linne and *Lygeum spartum*, Linne); jute (*Corchorus olitorius*, Linne); bamboo (*Bambusoideae* spp.; Linne); bagasse; or mixtures thereof.

In a specific case, the grass-like feedstock is miscanthus (*Miscanthus x giganteus*, Andersson).

Brief Description of the Drawings

Figure 1 - shows a block diagram of the process for production of cellulose pulp of very high whiteness from comminuted grass-like

feedstock according to the invention; key steps are: continuous digestion, disperging, continuous bleaching, optional disperging, dewatering which removes the black liquor, and washing of resulting pulp yielding white cellulose pulp.

The black liquor is optionally partially evaporated and further processed by electrolysis, isolating lignin and other non-cellulosic by-products, and to regenerate the cooking chemicals solution.

In the digestion and bleaching steps, microwave (MW)-heating can be optionally employed; marked with intermittent line.

Figure 2 - shows a block diagram of the process for production of cellulose pulp of very high whiteness according to the invention; with emphasis to additional steps: screening and fractionation and milling of cellulose pulp, which are performing optionally.

In the digestion and bleaching steps, microwave (MW)-heating can be optionally employed; marked with intermittent line.

Detailed Description of the Invention

The invention is related to an improved continuous process for production of cellulose pulp of very high whiteness, higher than 90%, of 10% w/w dry matter, and lignin content <5% w/w, from comminuted grass-like feedstock such as miscanthus (*Miscanthus x giganteus*, Andersson).

Such grass-like feedstock usually contains roughly 30-45% w/w of cellulose with 15-32% w/w of lignin; see literature reference 11:

11) C. Ververis, K. Georghiou, N. Christodoulakis, P. Santas, R. Santas: Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production, *Industrial Crops Prod.* **19** (2004) 245-254.

Large portion of this lignin has to be removed in a very mild manner to ensure maximal preservation of cellulose fibers to quality cellulose pulp for top-quality paper of very high whiteness.

According to the present invention, the process is performed in a continuous manner through several manufacturing phases, as shown in Figures 1 and 2:

(i) Preparation of the grass-like plant feedstock

The feedstock is prepared by comminuting, to produce a material with longitudinal size distributed from 5-30 mm and diameter of 0.1-2 mm. Comminution of the starting grass-like material is carried out by conventional devices for comminuting or supplied directly from the fields, if the crops were collected by suitable combine harvester equipped with adequate chopping device yielding the plant material of above-stated particles dimensions.

Primarily, the comminution should be performed in a mild manner yielding fibrous material predominantly comminuted along the fibers, in order to preserve them.

This is the reason why comminution is not shown in Figure 1, because it represents either conventional pre-treatment or may be even carried out during harvesting in the field.

Then, the comminuted material is subjected to dedusting by removal of fine, dusty, non-fibrous plant material, which would otherwise reduce the quality of resulting cellulose pulp. This is done by suitable fan which produces a strong air circulation that enable blowing away of fine light particles.

The latter fine dust does not enter into the process at all, thus saving significant amounts of digesting chemicals that would be otherwise spent through reaction of this material with sodium hydroxide (NaOH). Additionally, the effluents are not contaminated with such level of organic matter, what would significantly negatively affect the environment. This non-fibrous fine material mainly comes from central part of plant stalks. In the case of miscanthus, the percentage of this fraction is roughly 8-9% w/w.

Thus collected fine non-fibrous dust can be used in the process as a fuel in energy production or as raw material in manufacturing of xylan.

(ii) Continuous digestion of grass-like plant feedstock

Continuous digestion or cooking of a grass-like dust-free plant feedstock prepared in step (i) is performed in a continuous digester (1) formed as a longitudinal column, internally equipped with worm screw conveyor and a heating unit, where grass-like plant feedstock is continuously fed directly on the top of the said digester via conveyor (4).

In parallel with said feedstock feeding, the chemicals for digestion, sodium hydroxide (NaOH) and sodium chloride (NaCl), and fresh water and/or regenerated white liquor, are introduced continuously on the top of said digester (1); maintaining the digestion temperature from 70-120 °C and average composition of thus formed suspension during said continuous digestion is keeping within the following ranges:

(a) 0.50-2.00% w/w of NaOH;
(b) 0.50-1.50% w/w of NaCl;
(c) 10-15% w/w of grass-like plant feedstock; and
(d) process water; up to 100% w/w of the suspension;

wherein the weight percentages of ingredients being calculated on the weight of the whole suspension.

Under this digestion (cooking) of grass-like feedstock, the dissolution of non-cellulosic substances occurs during the mass transfer from one to the other side of the said longitudinal digester. The digestion or cooking phase lasts 1.5-3 hours.

Preferably, the continuous digestion process according to this invention is performed by introduction of cooking chemicals as concentrated aqueous solutions of 20-50% w/w sodium hydroxide (NaOH) and 10-30% w/w of sodium chloride (NaCl). Alternatively sodium hydroxide and sodium chloride solutions can be added as a previously prepared mixture.

Regarding the digestion process temperature, the preferred range is 90-100 °C.

(iii) Continuous disperging

The cooked cellulose pulp is continuously, by equal rate as being feedstock fed into the digester (1), discharged from the said digester (1), via conveyor, directly into disperger (5) to perform disperging phase (iii), where the suspended cellulose pulp is subjected to main disperging, yielding finely disperged/separated cellulose fibers.

The use of disperger (5) in this phase of the process is absolutely essential for high quality cellulose pulp.

(iv) Continuous bleaching

Thus obtained fine suspension of disperged cellulose pulp, after disperger (5), is further subjected to the bleaching phase (iv):

(a) without any removal of chemicals from the digestion phase (ii); and
(b) without the use of any additional NaOH for the bleaching purpose.

In the bleaching phase (iv), previously disperged cellulose pulp is continuously fed into the continuous bleaching reactor (6) which is, analogously to the digester (1), formed as a longitudinal column internally equipped with worm screw conveyor and a heating unit.

The bleaching is carried out with a solution of bleaching chemicals selected from the group comprising:

(a) 20-40% w/w aqueous hydrogen peroxide (H_2O_2) solution;
(b) 30-45% w/w aqueous waterglass or sodium silicate ($xNa_2O \bullet ySiO_2$) solution with the molar ratio $Na_2O:SiO_2$ = 1:1 to 3.3:1; and
(c) essentially without the use of any additional sodium hydroxide (NaOH).

These are introduced through manifold (7) into the bleaching reactor (6), maintaining the bleaching temperature from 70-100 °C, during 45 minutes to 1.5 h.

The average composition of thus formed suspension during whole bleaching process is keeping within the following ranges:

(a) 0.50-2.00% w/w of said H_2O_2 solution;
(b) 0.50-2.00% w/w of said $xNa_2O \bullet ySiO_2$ solution;
(c) 10-15% w/w of cellulose; and
(d) process water; up to 100% w/w of the suspension;

wherein the weight percentages of ingredients being calculated on the weight of the whole suspension. Preferably, the continuous bleaching process according to the present invention is carrier out at temperatures from 85-100 °C.

Additionally, bleaching chemicals are preferably introduced into the continuous bleaching reactor (6) separately in the form of concentrated aqueous solutions of 20-40% w/w of hydrogen peroxide (H_2O_2) and 30-45% w/w of sodium silicate ($xNa_2O \bullet ySiO_2$).

Optionally, after the bleaching process, the cellulose pulp can be additionally subjected to the treatment with optical brighteners in the manner that is well known in the art. Typical example of such optical brightener is Tinopal ABP-A liquid (from CIBA Specialty Chemicals Corporation), which contains 22-24% dry matter of fluorescent brightener from triazinyl stilbene-type. Such products are typically added at 0.25-0.50% w/w dosage to the dry matter content of cellulose pulp.

This treatment can be performed in order to further increase whiteness of the final cellulose when the highest possible, top-quality products are manufactured.

(v) Continuous disperging (optional)

Then the suspension of thus obtained bleached cellulose pulp, discharged from the bleaching step (iv), is optionally further subjected to additional disperging (phase v), through the disperger (8).

(vi) Continuous dewatering

In the further phase (vi), the cellulose pulp is transferred into the dewaterer (9), where the bleached and eventually additionally disperged cellulose pulp is dewatered, separated from the black liquor yielding:

(a) bleached cellulose pulp of 10-15% w/w dry matter; and
(b) the black liquor containing lignin and other cooking and bleaching by-products.

The black liquor from the dewatering step (vi) is transported via manifold (10) into the electrolytic reactor (19) for regeneration of cooking chemicals solution and isolation of lignin and other non-cellulosic by-products.

In the present invention, the term "black liquor" includes the process effluent from both digestion (ii) and bleaching (iv) phases;

it contains residual sodium hydroxide (NaOH), sodium chloride (NaCl), solubilized lignin, other non-cellulosic by-products, and eventually traces of remaining hydrogen peroxide.

Alternatively, the black liquor can be partially concentrated in evaporator (16) to yield regenerated water which is transported back to the washing step (vii) and concentrated back liquor which goes to the electrolytic reactor (19) via manifold (18).

(vii) Continuous washing process

The bleached cellulose pulp is additionally washed (phase vii) in the washing vessel (12) with additional fresh water, which is introduced through the manifold (13), giving:

(a) final bleached and washed cellulose pulp of very high whiteness, higher than 90%, of 10% w/w dry matter, and lignin content >5% w/w, which is transported out from the whole process through manifold (14); and

(b) additional amount of washing process water, which is transferred via manifold (15), together with the black liquor from the dewatering step (vi), which is transported via manifold (10), into the electrolytic reactor (19).

In the present invention, the term "washing process water" includes the process effluent from the continuous washing process (vii phase); it contains residuals of the black liquor that always remains adsorbed on cellulose fibers within the pulp that comes out from the dewatering phase (vi). Therefore, the washing process water is more likely as very diluted black liquor.

(viii) Continuous electrolytic regeneration of cooking chemicals solution and isolation of lignin and other non-cellulosic by-products

Continuous electrolytic regeneration of cooking chemicals solution (white liquor) and isolation of lignin and other non-cellulosic by-products is performed either:

(a) directly with combined black liquor coming via manifold (10) and washing process water coming via manifold (15), without previous concentration in evaporator (16); or

(b) optionally, combined black liquor and washing process water are partially concentrated in the evaporator (16) yielding concentrated black liquor that is transferred via manifold (18) into the electrolytic reactor (19).

In the case of optional concentration of the black liquor, optimal degree of the black liquor concentration is preferably up to 0.9-1.05 w/w of sodium (as Na^{+}) in the concentrated black liquor that enters the electrolytic reactor (19).

The term "evaporator" involves not only classical evaporation devices which are based on either distillation or vacuum distillation, but also all other means of water removal from the aqueous solutions, e.g. by reverse osmosis, ion-exchange process, electrodeionization, etc.

In the electrolytic reactor (19), either original ("as is") combined black liquor (a) or concentrated black liquor (b) is subjected to electrolysis with direct electric current (DC) between two electrodes, at electric potential of 3-30 V, and electric current density of 1-10 A/dm^2, at 10-95 °C, wherein the lignin and by-products are separated on the top of the electrolyte solution in the anode compartment, and continuously removed from the electrolytic reactor.

The electrolytic lignin removal is performed in the electrolytic cell similar or identical to those disclosed in the literature reference 10, wherein cathode and anode compartments are separated by a suitable semi-permeable membrane or diaphragm.

Electrodes, cathode and anode, are made from suitable electro-conductive materials resistant to highly reactive chemicals formed in their compartments, e.g. to NaOH of high pH value. Such suitable materials are: metals such as carbon steel or stainless steels, graphite, magnetite, etc.

Preferably, cathode is made from a carbon steel, e.g. of type A36, or stainless steels, e.g. of types AISI 304, 316, 321, whilst anode is formed from graphite or magnetite.

Electrodes can be formed in various shapes, of which plates and wire mesh are preferred.

Diaphragm is made from materials selected from the group comprising: asbestos, rock wool (stone wool), Portland cement, aluminium oxide (Al_2O_3), titanium dioxide (TiO_2), zirconium dioxide (ZrO_2), polyethylene (PE), polyetersulfone (PES), polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE; Teflon^R), polyvinylidene fluoride (PVDF), sulfonated polytetrafluoroethylene (Nafion^R), clay and sodium silicate, from combinations of said materials, or from other suitable chemically resistant materials.

Preferably, the electrolytic lignin removal and white liquor regeneration is conducted at electric potential of 3-10 V and electric current density of 3-7 A/dm^2.

The alkaline black liquor from the cellulose-manufacturing process is introduced into the anode compartment.

During electrolysis of the black liquor solution the lignin and other by-products are separated on the top of the electrolyte solution from the anode (+) compartment, and are removed out from the process by conventional mechanic means, via conveyor or so.

Separation of lignin within the anode (+) compartment is facilitated by the evolution of gaseous oxygen (O_2) as a by-product of accompanied water electrolysis.

In the same time, in the cathode (-) compartment the main reaction is evolution of hydrogen (H_2), which is accompanied with increasing concentration of sodium hydroxide (NaOH). Thus regenerated sodium hydroxide solution from the cathode compartment, together with sodium chloride (NaCl) which remains in the solution, is transported back to the digester (1) via manifold (21).

The resulting electrolyte solution with regenerated sodium hydroxide (NaOH) and sodium chloride (NaCl) solution, representing the white liquor, is regenerated back to the digesting/cooking process, via manifold (21), to the continuous digester (1), closing the whole cellulose-manufacturing process.

In the present invention, the term "white liquor" includes the process effluent from the phase (viii) of the continuous electrolytic regeneration of cooking chemicals, NaOH and NaCl, solution. It contains mainly diluted sodium hydroxide and sodium chloride, with trace amounts of lignin and other non-cellulosics originating from the black liquor.

The lignin is separating at the top of the electrolyte solution in the cathode compartment and is continuously removing via conventional conveyor type transporter (20).

The presence of these trace amounts of residual plant-occurring ingredients does not influence the performance of overall process and the quality of the final cellulose pulp upon the use of this regenerated white liquor as the only process water during repeated process cycles.

The term "electrolytic reactor" in the present invention includes single or a battery (series) of several or large number of combined electrolytic cells. This depends on the capacity or scale of cellulose pulp manufacturing by using the process according to this invention. For instance, larger manufacturing facility may comprise a series of 10-100 electrolytic cells. In the case of high tonnage manufacturing facility, such "electrolytic reactor" can comprise several hundreds of such electrolytic cells.

Optionally, the process for production of cellulose pulp, of very high whiteness, according to the present invention further comprises the manufacturing steps of screening, fractionation, and milling.

The whole cellulose manufacturing process according to the present invention through phases (i)-(vii) is presented in Scheme 1.

(ix) <u>Screening and fractionation of cellulose pulp</u>

In these operations the diluted suspension from the step (viii) is further processed through a screening and fractionation device (22) equipped with 0.1-0.5 mm sieve, yielding two fractions;

(a) the first fraction that does not pass through the 0.1-0.5 mm screen; and
(b) the second fraction that passes through the 0.1-0.5 mm screen, which is considered as a good cellulose pulp suitable for manufacturing of top-quality paper or cellulose sheets, which is transported out from the whole process through manifold (23).

(x) <u>Milling of cellulose pulp</u>

This is required to process the (a) fraction of the cellulose pulp from the step (ix) through one or two subsequent milling steps by using the pulp mills (24, 25), yielding cellulose pulp which is transferred, via manifold (26), back to the screening and fractionation device (22). In this manner, whole amount of eventually improper cellulose pulp fraction is processed to the desired final product that comes out from the whole process via manifold (23).

The whole cellulose manufacturing process according to the present invention through phases (i)-(vii) including the optional phases (ix) and (x) is presented in Scheme 2.

The use of alternative means of heating

A continuous process for production of cellulose pulp, of very high whiteness, according to the present invention can be performed by employing the microwave (MW) heating in the continuous digester (1) and/or continuous bleaching reactor (6) in the manner that is known in the art. In this case, the heating units in the continuous digester (1) and/or continuous bleaching reactor (6) are microwave (MW)-generating magnetrons, or series of the magnetrons.

Grass-like feedstock

The grass-like feedstock that can be used as starting raw material for the process of the present invention includes stems of plant species selected from the group of: wheat (*Triticum* vulgare, Linne); rice (*Oryza* sativa, Linne); barley (*Horedum vulgare*, Linne); oat (*Avena sativa*, Linne); flax (*Linum usitatissimum*, Linne); maize (*Zea mays*, Linne); millets: proso millet (*Panicum miliaceum*, Linne), pearl millet (*Pennisetum glaucum*, Linne), browntop millet (*Panicum ramosum*, Linne), and barnyard (*Echinochloa frumentaceae*, Linne); triticale (x *Triticosecale*, Wittm. ex A. Camus); buckwheat (*Fagopyrum esculentum*, Moench); miscanthus (*Miscanthus x giganteus*, Andersson); switchgrass (*Panicum virgatum*, Linne); sorghum (*Sorghum* species, Linne); common reed (*Phragmites australis*, Cav.), giant reed (*Arundo donax*, Linne), burma reed (*Neyraudia reynaudiana*, Kunth.), reed-mace (*Typha* spp., Linne), paper reed (*Cyperus papyrus*, Linne), bur-reed (*Sparganium* spp., Linne), thatching reed (*Thamnochortus insignis*, Linne); esparto grass (*Stipa tenacissima*, Linne and *Lygeum spartum*, Linne); jute (*Corchorus olitorius*, Linne);

bamboo (*Bambusoideae* spp., Linne); bagasse; or mixtures thereof. The preferred grass-like feedstock is miscanthus (*Miscanthus x giganteus*, Andersson).

Results of cellulose analyses manufactured by the process from the present invention

The superior characteristics of cellulose manufactured by the present invention can be clearly seen when the results of analyses of resulting paper samples are compared with also good cellulose manufactured by the similar process disclosed in the closest prior art; see literature reference 9.

The results of cellulose analysis and comparison with the same parameters for the cellulose obtained by the process from the closest prior art is presented in Table 1.

Table 1. Comparison of paper properties prepared from cellulose obtained by the process from the present invention and from cellulose obtained by the process from the closest prior art, reference 9 (as the control).

No.	Parameter	Method	Unit	Cellulose from prior art,ref. 9[a]	Cellulose from the invention[b]
1	Lignin content	TAPPI T222	%	<5.0[c]	4.8
2	Basis weight	EN ISO536:2012	g/m^2	96.11	100.92
3	Tensile strength	EN ISO1924-2:2009	km	4.800	5.410
4	Bursting strength	EN ISO2758:2014	$kPam^2/g$	2.95	3.25
5	Opacity	EN ISO2471:2011	%	83.40	85.13
6	Brightness	EN ISO2470-1:2013	%	<80.00[d]	97.94
7	CMT (0)	ISO7263:2011	N	~152	188.8
8	CMT (30)	ISO7263:2011	N	n.a.	150.2

[a] The paper sample from the control cellulose pulp was manufactured by the process from the closest prior art (see reference 9); in the bleaching step, H_2O_2 + NaOH was employed in as the bleaching system. The concentration of H_2O_2 was kept the same as in the present invention.

[b] The paper sample from the cellulose pulp prepared by the process from the present invention.

[c] The content of lignin in the cellulose pulp is generally <5% w/w, calculated on dry matter, as this ensure a good mechanical properties of resulting paper.

[d] Based on previous experiments.

n.a. = not analyzed.

Experimental results showed significantly better mechanicals properties (tensile and bursting strengths) of the cellulose and thus resulting paper at the same (comparable) grammage (basis weight around 100 g/m2. Tensile strength was 5.410 versus 4.800, what represents +13% improvement, and bursting strength 3.25 versus 2.95, what is +10% enhanced. These results clearly suggest better mechanical properties of the cellulose from the present invention what is probably ensured by improved preservation of original cellulose fibers during processing.

Additionally brightness (whiteness) of cellulose was significantly improved to over 90% (97.94%) versus maximally 80% that could be achieved by the use of the process from the closest prior art (literature reference 9).

Eventual changes of the process parameters can result in some further improvement of key quality parameters of resulting cellulose, but such changes are considered to be within the scope of this invention.

Industrial Applicability

The present invention is obviously industrial applicable.

Furthermore, the process from the present invention is characterized by the following key features:

(i) very mild digesting and bleaching process for grass-like feedstock what result in very preserved cellulose pulp with improved mechanical properties, lignin content of <5% w/w, and whiteness >90%, making it suitable for production of top-quality papers;

(ii) mild dispreging between digesting and bleaching phases, essentially without any removal of the black liquor after the digesting phase;

(iii) wherein both digesting and bleaching processes are technologically optimized to ensure minimal chemicals consumption;

(iv) where bleaching process in performed by the novel hydrogen peroxide (H_2O_2)-sodium silicate ($xNa_2O{\bullet}ySiO_2$) system, essentially without any sodium hydroxide (NaOH) use; and

(v) integrated and efficient electrolytic lignin removal from the black liquor solution with accompanied sodium hydroxide (+ NaCl) solution regeneration, which is reused back in the cooking process as a white liquor, thus closing the whole manufacturing cycle without any significant waste and environmental impact.

List of references

1 - continuous digester
2 - manifold for introducing fresh water
3 - manifold for introducing digesting chemicals
4 - conveyor for feeding comminuted grass-like feedstock
5 - disperger
6 - continuous bleaching reactor; essentially the same as continuous digester
7 - manifold for introducing bleaching chemicals
8 - disperger; this one is optional; marked with intermittent line
9 - dewaterer

10 – manifold for transport of the black liquor from dewaterer to the electrolytic reactor for lignin removal, or optionally, to the evaporator 16

11 – manifold for transport of dewatered cellulose pulp into the washing vessel 12

12 – cellulose pulp washing vessel

13 – manifold for fresh water introduction

14 – manifold for output of final white cellulose pulp

15 – manifold for transport of spent process water from cellulose pulp washing into to the electrolytic reactor for regeneration, or optionally, to the evaporator 16

16 – optional evaporator; for partial concentration of combined black liquor + washing process water

17 – optional manifold for transport of regenerated clean water from evaporator back to the cellulose washing vessel

18 – manifold for transport of the black liquor into the electrolytic reactor 16, or optionally, concentrated black liquor if the evaporator is employed

19 – electrolytic reactor for lignin and other by-product removal

20 – manifold for output of lignin and other non-cellulosic by-products

21 – manifold for transporting regenerated cooking chemicals back into the digester 1

22 – screening and fractionation device

23 – manifold for output of white cellulose pulp when optional screening and fractionation is preformed

24 – pulp mill

25 – pulp mill

26 – manifold for transporting milled white cellulose pulp back to the screening and fractionation device

CLAIMS

1. A continuous process for production of cellulose pulp of very high whiteness from grass-like plant feedstock, where said process comprising the steps of:
   (i) preparing the grass-like plant feedstock by comminuting to produce a feedstock with longitudinal size distributed from 5-30 mm and diameter of 0.1-2 mm, and with removed fine dusty particles by dedusting of said feedstock with fan;
   (ii) continuous digestion of a grass-like dust-free plant feedstock prepared in step (i) in a continuous digester (1) formed as a longitudinal column internally equipped with worm screw conveyor and a heating unit; where grass-like plant feedstock is continuously fed directly on the top of the said digester via conveyor (4);

characterized by that

in parallel with said feedstock feeding in, the chemicals for digestion: NaOH, NaCl, and fresh water and/or regenerated white liquor; are introduced continuously on the top of said digester (1); maintaining the digestion temperature from 70-120 °C and average composition of thus formed suspension during said continuous digestion is keeping within the following ranges:

(a) 0.50-2.00% w/w of NaOH;
(b) 0.50-1.50% w/w of NaCl;
(c) 10-15% w/w of grass-like plant feedstock; and
(d) process water; up to 100% w/w of the suspension;

wherein the weight percentages of ingredients being calculated on the weight of the whole suspension; and where a dissolution of non-cellulosic substances from the grass-like plant feedstock occurs during the mass transfer from one to the other side of the said longitudinal digester that lasts 1.5-3 hours;

(iii) where cooked pulp is continuously, by equal rate as being feedstock fed into the digester (1), discharged from the said digester (1), via conveyor, directly into disperger (5), where the suspended cellulose pulp is further subjected to main disperging, yielding finely disperged cellulose fibers;

(iv) where fine suspension of disperged cellulose pulp from step (iii) is further subjected to bleaching:

(a) without any removal of chemicals from the digestion phase (ii); and

(b) without the use of any additional NaOH for the bleaching purpose;

where disperged cellulose pulp is continuously fed into the continuous bleaching reactor (6) which is formed as a longitudinal column equipped with worm screw conveyor and a heating unit; and

where bleaching chemicals are selected from the group comprising:

(a) aqueous hydrogen peroxide /H_2O_2/ solution with 20-40% w/w H_2O_2; and

(b) aqueous sodium silicate /$xNa_2O \bullet ySiO_2$/ solution with 30-45% w/w of combined Na_2O+SiO_2, with the molar ratio $Na_2O:SiO_2$ = 1:1 to 3.3:1;

and where said chemicals are introduced through manifold (7) into the bleaching reactor (6), maintaining the bleaching temperature from 70-100 °C, during 45 minutes to 1.5 h, and average composition of thus formed suspension during whole bleaching process is keeping within the following ranges:

(a) 0.50-2.00% w/w of said H_2O_2 solution;

(b) 0.50-2.00% w/w of said $xNa_2O \bullet ySiO_2$ solution;

(c) 10-15% w/w of cellulose; and

(d) process water; up to 100% w/w of the suspension;

wherein the weight percentages of ingredients being calculated on the weight of the whole suspension;

(v) the suspension of thus obtained bleached cellulose pulp, discharged from the bleaching step (iv), is optionally further processed through the disperger (8); and then transferred into the dewaterer (9);

(vi) where the bleached and eventually additionally disperged cellulose pulp from the step (v) is dewatered, separated from the black liquor yielding:

(a) bleached cellulose pulp of 10-15% w/w dry matter; and

(b) the black liquor containing lignin and other cooking and bleaching by-products; and

(vii) the bleached cellulose pulp is additionally washed in the washing vessel (12) with additional fresh water, which is introduced through the manifold (13) giving:

(a) final bleached and washed cellulose pulp of very high whiteness, higher than 90%, of 10% w/w dry matter, and lignin content <5% w/w, which is transported out from the whole process through manifold (14); and

(b) additional amount of washing process water which is transferred via manifold (15), together with the black liquor from the dewatering step (vi), which is transported via manifold (10) into the electrolytic reactor (19);

(viii) where the black liquor and washing process water are further subjected to electrolysis with direct electric current between two electrodes, at electric potential of 3-30 V, and electric current density of 1-10 A/dm^2, at 10-95 °C, wherein the lignin and by-products are separated on the top of the electrolyte solution in the anode compartment, and continuously removed from the electrolytic reactor; and

wherein the resulting electrolyte solution with regenerated NaOH and NaCl solution, representing the white liquor, is regenerated from the cathode compartment back to the cooking process, via manifold (21), to the continuous digester (1), thus closing the whole cellulose-manufacturing process.

2. A continuous process for production of cellulose pulp according to the claim 1, **characterized by that** it further comprises the steps of:

(ix) screening and fractionation, where diluted suspension from the step (viii) in claim 1, is processed through a screening and fractionation device (22) equipped with 0.1-0.5 mm sieve, yielding two fractions;

(a) the first fraction that does not pass through the 0.1-0.5 mm screen; and

(b) the second fraction that passes through the 0.1-0.5 mm screen, which is considered as a good cellulose pulp of very high whiteness, higher than 90%, suitable for manufacturing of top-quality paper or cellulose sheets, which is transported out from the whole process through manifold (23); and

(x) where fraction (a) of the cellulose pulp from the step (ix) is subjected to one or two subsequent processing through the pulp mills (24, 25) yielding the cellulose pulp, which is transferred, via manifold (26), back to the screening and fractionation device (22).

3. A continuous process for production of cellulose pulp according to any of preceding claims **characterized by that** the chemicals for digestion in step (ii) claim 1 are introduced as a mixture of concentrated aqueous solutions of 20-50% w/w NaOH and 10-30% w/w of NaCl.

4. A continuous process for production of cellulose pulp according to any of preceding claims **characterized by that** the digestion temperature is maintained in the range 90-100 °C.

5. A continuous process for production of cellulose pulp according to any of preceding claims **characterized by that** the bleaching temperature is maintained in the range 85-100 °C.

6. A continuous process for production of cellulose pulp according to any of preceding claims **characterized by that** the heating units in the continuous digester (1) and continuous bleaching reactor (6) are microwave (MW)-generating magnetrons.

7. A continuous process for production of cellulose pulp according to any of preceding claims **characterized by that** the combined black liquor and washing process waters that come out from the process steps (vi) and (vii) in claim 1 via manifolds (10) and (15) are optionally concentrated up to the content of total sodium 0.90-1.05% w/w in the evaporator (16) before further processing in electrolytic reactor (19).

8. A continuous process for production of cellulose pulp according to any of preceding claims **characterized by that** the electrolytic lignin removal and white liquor regeneration in the step (viii) of claim 1 within the electrolytic reactor (19) is conducted with graphite anode and carbon steel or stainless steels cathode, at electric potential of 3-10 V, electric current density of 3-7 A/dm^2.

9. A continuous process for production of cellulose pulp according to any of preceding claims, **characterized by that** the grass-like feedstock includes stems of plant species selected from the group of: wheat /*Triticum* vulgare, Linne/; rice /*Oryza* sativa, Linne/; barley /*Horedum vulgare*, Linne/; oat /*Avena sativa*, Linne/; flax /*Linum usitatissimum*, Linne/; maize /*Zea mays*, Linne/; millets: proso millet /*Panicum miliaceum*, Linne/, pearl millet /*Pennisetum glaucum*, Linne/, browntop millet /*Panicum ramosum*, Linne/, and barnyard /*Echinochloa frumentaceae*, Linne/; triticale /x *Triticosecale*, Wittm. ex A. Camus/; buckwheat /*Fagopyrum esculentum*, Moench/; miscanthus /*Miscanthus x giganteus*, Andersson/; switchgrass /*Panicum virgatum*, Linne/; sorghum /*Sorghum* species, Linne/; common reed /*Phragmites australis*, Cav./, giant reed /*Arundo donax*, Linne/, burma reed /*Neyraudia reynaudiana*, Kunth./, reed-mace /*Typha* spp., Linne/, paper reed /*Cyperus papyrus*, Linne/, bur-reed /*Sparganium* spp., Linne/, thatching reed /*Thamnochortus insignis*, Linne/; esparto grass /*Stipa tenacissima*, Linne and *Lygeum spartum*, Linne/; jute /*Corchorus olitorius*, Linne/, bamboo /*Bambusoideae* spp., Linne/, bagasse, or mixtures thereof.

10. A continuous process for production of cellulose pulp according to the claim 8, **characterized by that** the grass-like feedstock is miscanthus /*Miscanthus x giganteus*, Andersson/.

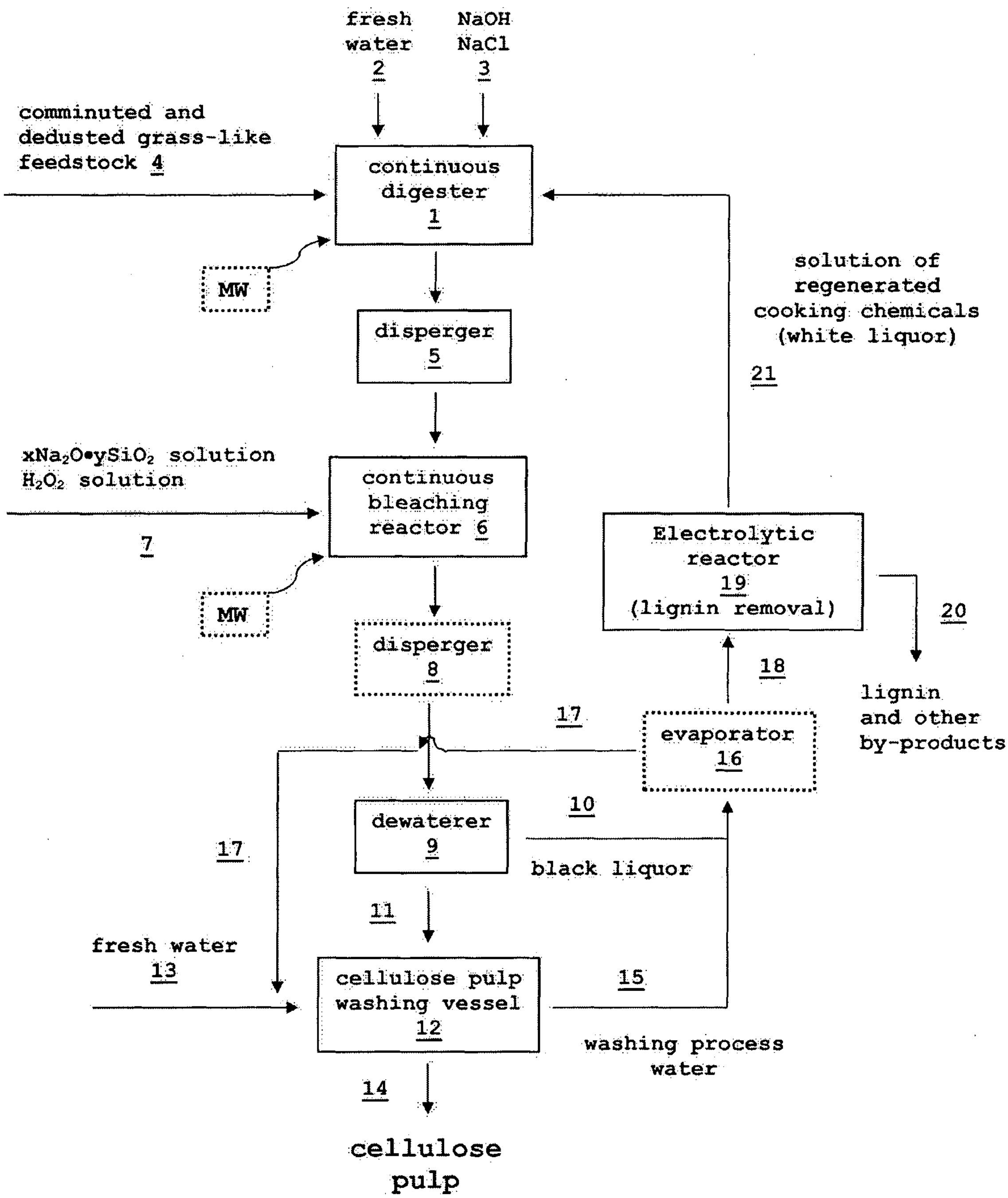
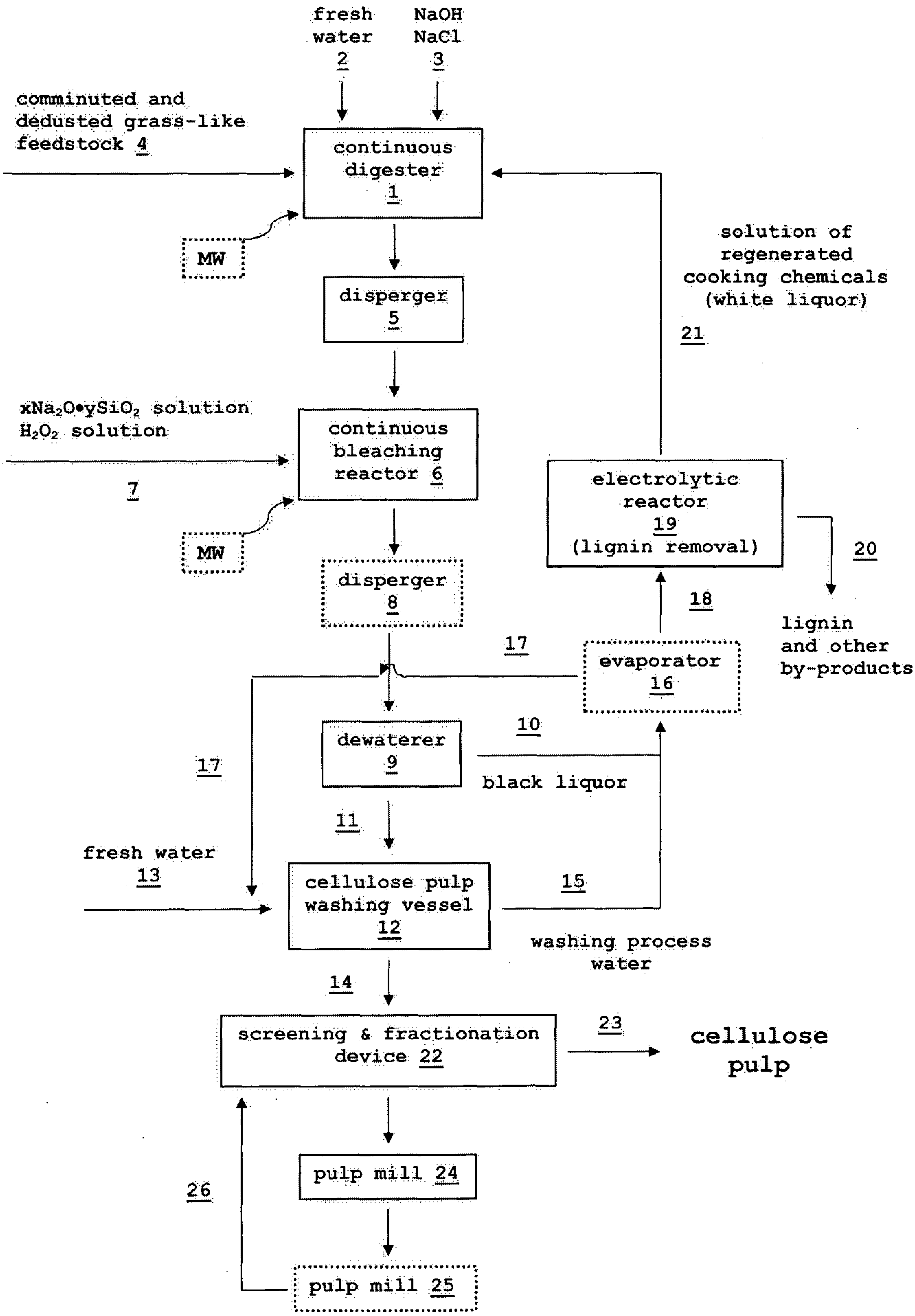

fresh water 2
NaOH NaCl 3
comminuted and dedusted grass-like feedstock 4
continuous digester 1
MW
disperger 5
solution of regenerated cooking chemicals (white liquor)
21
xNa2O•ySiO2 solution H2O2 solution
7
continuous bleaching reactor 6
MW
disperger 8
Electrolytic reactor 19 (lignin removal)
20
18
lignin and other by-products
17
evaporator 16
17
dewaterer 9
10
black liquor
11
fresh water 13
cellulose pulp washing vessel 12
15
washing process water
14
cellulose pulp

Figure 1



fresh water 2
NaOH NaCl 3
comminuted and dedusted grass-like feedstock 4
continuous digester 1
MW
disperger 5
solution of regenerated cooking chemicals (white liquor)
21
xNa2O•ySiO2 solution
H2O2 solution
7
continuous bleaching reactor 6
MW
electrolytic reactor 19 (lignin removal)
20
disperger 8
18
lignin and other by-products
17
evaporator 16
dewaterer 9
10
black liquor
17
11
fresh water 13
cellulose pulp washing vessel 12
15
washing process water
14
screening & fractionation device 22
23
cellulose pulp
pulp mill 24
26
pulp mill 25

Figure 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/HR2016/000014

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21C3/02 D21C9/10 D21C9/16 D21C11/00 D21H11/12
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

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.
A	WO 94/12720 A1 (KAMYR AB [SE]; BACKLUND AAKE [SE]; NILSSON BENGT [SE]; STIGSSON LARS [) 9 June 1994 (1994-06-09) claims 1-11	1-10
A	US 3 950 217 A (REEVE DOUGLAS W) 13 April 1976 (1976-04-13) column 10, line 57 - line 60; figure 1	1-10
A	US 3 698 995 A (RAPSON WILLIAM H) 17 October 1972 (1972-10-17) claim 1	1-10
A	WO 85/05386 A1 (FLINCK KARL EVERT) 5 December 1985 (1985-12-05) Page 9, last paragraph	1-10

-/--

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"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
11 November 2016	24/11/2016

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	Ponsaud, Philippe

4

INTERNATIONAL SEARCH REPORT

International application No
PCT/HR2016/000014

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2013/135957 A2 (UPM KYMMENE CORP [FI]) 19 September 2013 (2013-09-19) claim 1; figure 1	1-10

4

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/HR2016/000014

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 9412720	A1	09-06-1994	AT	162568	T	15-02-1998
			AU	681613	B2	04-09-1997
			BR	9307572	A	01-06-1999
			CA	2150254	A1	09-06-1994
			DE	69316652	D1	26-02-1998
			DE	69316652	T2	04-06-1998
			EP	0672208	A1	20-09-1995
			ES	2114171	T3	16-05-1998
			FI	952596	A	29-05-1995
			JP	H08504005	A	30-04-1996
			NO	952152	A	31-05-1995
			SE	470538	B	25-07-1994
			US	6336994	B1	08-01-2002
			WO	9412720	A1	09-06-1994
US 3950217	A	13-04-1976	CA	1008204	A	12-04-1977
			ES	421470	A1	01-10-1976
			FI	58659	B	28-11-1980
			FR	2210695	A1	12-07-1974
			NO	142409	B	05-05-1980
			SE	400997	B	17-04-1978
			US	3950217	A	13-04-1976
US 3698995	A	17-10-1972	CA	956754	A	29-10-1974
			GB	1217833	A	31-12-1970
			US	3698995	A	17-10-1972
WO 8505386	A1	05-12-1985	AU	4404285	A	13-12-1985
			EP	0214982	A1	25-03-1987
			WO	8505386	A1	05-12-1985
WO 2013135957	A2	19-09-2013	CN	104169494	A	26-11-2014
			FI	20125262	A	13-09-2013
			RU	2014136220	A	27-04-2016
			UY	34672	A	31-10-2013
			WO	2013135957	A2	19-09-2013