



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 707 668 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
04.10.2006 Bulletin 2006/40

(51) Int Cl.:
D21C 3/00 (2006.01) D21C 9/147 (2006.01)

(21) Application number: **03767376.1**

(86) International application number:
PCT/CN2003/001121

(22) Date of filing: **25.12.2003**

(87) International publication number:
WO 2005/064076 (14.07.2005 Gazette 2005/28)

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**

• **XIE, Laisu**
Dagu Nanlu,
Tianjin 300222 (CN)

(71) Applicant: **Mei, Xiuquan**
Haidian District
Beijing
100089 (CN)

(74) Representative: **Gerbino, Angelo et al**
Jacobacci & Partners S.p.A.
Corso Emilia 8
I-10152 Torino (IT)

(72) Inventors:
• **MEI, Xiuquan**
Haidian District,
Beijing 100089 (CN)

(54) **CLOSED CYCLE ZERO DISCHARGE OXIDIZING PULPING PROCESS**

(57) The object of the present invention is to provide a fully-closed, zero discharging and clean oxidizing pulping process and the preparation method thereof. In accordance with the present invention, it employs active oxygen free radicals generated by electron reduction reaction of molecular oxygen in an ion reactor to transform and separate lignin, to change chromophoric groups in the intercellular space and to obtain paper pulp. The conventional pulping technologies which use harmful pollut-

ing chemicals such as acid, alkaline, chlorine, anthraquinone and so on are basically changed in the present invention. The cooking and bleaching process, which generate severe pollution, can be avoided. The abundant annually grown fiber materials can be utilized in this process, and water and energy can be saved. The present invention can reduce production cost and have excellent social, economic and environmental benefits.

EP 1 707 668 A1

Description**Field of the invention**

[0001] The invention relates to a clean, fully-closed, zero-discharging pulping process by oxidation and the preparation method thereof. In particular, it relates to a clean pulping process having the characteristics of close-loop, self-cycling, no acid used, no alkali used, no chlorine used, no anthraquinone used, no cooking needed, no bleaching needed, no draining and no pollution.

Background of the invention

[0002] Short supply of papermaking materials is a problem faced by the pulping & papermaking industry in a long term and occurs not in a single district but in the whole world. Forest acts as the lung of earth that can absorb carbon dioxide and produce oxygen in addition to the effects on the conservation of water resources, prevention of soil erosion, and adjustment of climate. And it has both ecological and economic values. However, it is now decreasing at a rate of $700 \times 10^8 \text{ m}^2$ per year and tropical rain forest is decreasing at a rate of $50 \times 10^4 \text{ m}^2$ per minute. If the illegal ruinous exploitation is not strictly restricted, with the increasing of the whole world population, human beings may have to face the dilemma of no adequate oxygen to breathe 40 years later.

[0003] According to a comparison of the China Forestry Statistical Yearbook in 1999 with the one in 2000, the decreasing rate of forest area is: Ten Major Forestry Ecological Programs -12.9%, Naturally Formed Forest Conservation Program -10.7%, area of the hillside closed for regeneration of forest -6.33%, protection forest -24.75%, economic plantations -3.82% and forest for commercial timber -14.07%.

[0004] Based on the plant fiber chemistry, non-wood cellulose materials can be categorized as: 1. gramineous fiber materials; 2. phloem fiber materials; 3. cotton linters fiber materials; 4. leaf fiber materials. And the holocellulose content of non-wood fiber materials is 48%-84%. The length of most non-wood fiber is longer than that of wood fiber. Cellulose is the main material used in papermaking. Cellulose extracted either from wood or from non-wood materials can be used as supporting materials of paper and for the production of raw materials of middle or high quality pulp. It is demonstrated that in the fiber of non-wood materials such as cotton stalk, all kinds of chemical components are similar to that of broad-leaved wood and needle-leaved wood.

[0005] China is an agricultural country and also a cotton-producing country. The yield of annual plant resource is about 160 million tons (t), which is comparable to the wood resource. During the "Ten-Five" Plan, the growing area in the major cotton-producing regions of China is expected to be stabilized at a level of 6 million hm^2 in 2010. There are 34.2 million tons of high quality cotton stalks annually. Based on the data in textbook, output of cotton stalk pulp is 24.282 million tons. If the utilization ratio is 20%, the output is 4.856 million tons/year, however, heretofore, the utilization ratio of the annual plant resource resembling the broad-leaved wood is less than 1%. 235 million tons of non-wood fiber materials can be extracted from cornstalk, wheat straw, rice straw (in accordance with Agriculture Statistical Yearbook of 2000, the yield thereof has already reached 470 million tons). Now utilization ratio of the vast pulping resource of annual plant is less than 5%. These annual plant resources are called agricultural green waste in the United States, and are called green annual plant resource in China.

[0006] In "Pulping Technology and Equipment" published by China Light Industry Publishing in 2000, the contents of holocellulose of various fiber materials determined by sodium chlorite are disclosed, as shown in table 1.

Table 1 unit: weight %

Materials	Production Place	Holocellulose	Materials	Production Place	Holocellulose
spruce	xiaoxinganling	73. 0	Wheat straw	Hebei	71. 3
korean pine	daxinganling	69. 6	Sugarcane residue	Guangdong	75. 6
populus	henan	81. 6	Chinese alpine rush	Guangxi	76. 7
xiaozuanyangica			Sorghum stalk	Hebei	66. 4
bambusa oldhami	zhejiang	69. 5	Corn stalk	Hebei	84. 9
Bambusa eduldoides	Guangdong	67. 2			
phragmites communis	Hubei	75. 4	Achnatherum	Ningxia	79. 8
miscanthus sinensis	Hubei	76.6	Deyounia angstyolia	Heilongjiang	74.9

EP 1 707 668 A1

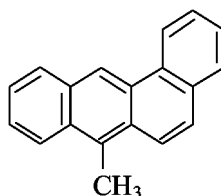
(continued)

Materials	Production Place	Holocellulose	Materials	Production Place	Holocellulose
cotton stalk	Jiangsu	75. 1	Chinese silvergrass	Sichuan	84. 3
rice straw	Hebei	64. 0			

[0007] In "Plant Fiber Chemistry" that published by China Light Industry Publishing in 2001, data for chemical analysis of cotton stalk materials (weight%) and average length of fibers (mm) are listed in table 2.

Part of cotton stalk	moisture	ash	extract				Sodium chlorite holocellulose	Klason Lignin	Polypentose	Pectin	Average fiber
			Cold water	Hot water	1%NaOH	Phenylalcohol					
Cotton stalk peel	6.12	6.12	18.34	23.66	43.57	2.7	75.57	16.84	23.26	9.64	2.46
Cotton cane	7.87	2.05	3.71	5.02	21.36	1.68	76.32	21.31	18.07	1.42	1.08
Full cotton stalk	8.12	3.15	7.68	9.74	28.72	1.94	75.95	20.17	19.27	4.25	1.68

[0008] It is well-known that papermaking worldwide still uses the traditional process invented before 100 years in which strong acids, strong alkalis, strong chlorine are used and black liquor is drained without restraint. The traditional process has seriously impacted the environment that human beings rely on for living. In recent years anthraquinone is introduced in papermaking in Japan, India, Canada etc. Anthraquinone is a fused polycyclic aromatic hydrocarbon of arenes. All of the fused polycyclic aromatic hydrocarbons have been confirmed to be carcinogenic. For instance, a known carcinogen structure made of anthracene is as follows:



10-methyl-1, 2-benzanthracene or ethylene-1, 2-benzanthracene

[0009] The order relating to the prohibition of chlorine in pulp bleaching was promulgated by Environmental Protection Agency (USA) in April 2000. More recently, 54% of papermaking companies in the world are fixing their eyes on ClO₂ as the bleaching agent. 91% of ClO₂ may produce dioxine and other organic compounds, nevertheless, the remaining 9% is discharged as Cl₂, which does harm the environment that human beings rely on.

[0010] The oxidizing bleaching of pulp can date back to the early 1950's. Oxygen was first found to have a bleaching ability by Soviet wood chemist Nikieih and ARim in 1952. Twelve years later, magnesium salts are found to be able to avoid cellulose to be oxidized and degraded by French scientist Rebeve et al in 1964. Laboratories were established one after another in three countries (U.S., France and Sweden) in 1970. In the same year, the first chlorine dioxide bleaching plant of the world was constructed in Enstrd of South Africa. In 1972, oxygen bleaching plant with a capacity of 12t/d was set up in the U.S. and the technology was patented, however, it was not put into service due to the great loss of cellulose, high energy consumption, high water consumption and high production cost. Twenty-seven years later, Gerogelude Company in France (1999) and Prinsell Company in America (2001) successively used the combination of ClO₂ and O₃ for bleaching. But chlorine pollution was not gotten rid of. Referring to the patents before March, 2002 of all over the world, the papermaking worldwide still employed the seriously polluting cooking process with strong acid, strong alkali and strong chlorine, and still utilized the seriously polluting bleaching process with chlorine. Treatment of lignin chromophores still relied on the traditional process of separation and degradation of lignin used 100 years ago. For this reason, papermaking in the world has become an important object of concern for the environment protection organization.

[0011] Pulp bleaching with ClO₂ and O₃ (CN1212310A) invented by France Liquid Air Company was published on March 31, 1999. Pulping process using cornstalk and other non-wood fiber materials (CN1371439A) invented by North Carolina State University of U.S. was published on Sep 25, 2002. Other patent applications include: a pulping process using non-wood material and its preparation equipment (CN1407172A) invented by Japan Business Corporation published on April 2, 2003, a pollution-free pulping method (CN1198492) invented by Shandong Weichang Normal University, a pulping method without alkali (CN1229155) and a pulp bleaching electrochemical technology of polyoxometallate (CN1458075) etceteras.

[0012] Referring to all above patents, some are related to bleaching method without chlorine, some aim at reducing the amount of acid, alkali and chlorine used, some are using ozone instead of chlorine, some are using alkali, anthraquinone and peroxide acid. Until March, 2002, there is no method which can finish degradation of lignin without using acid, alkali, and no method which eliminates the use of acid, alkali and chlorine completely, which implies that the pollution problem has not been resolved in these patents. The present invention solves the pollution problem in papermaking. The invention solves the problem of using strong acid, strong alkali, chloride and anthraquinone during the whole process of degradation of lignin and bleaching. All wastewater produced by papermaking is not drained outwards, thereby forms a fully-closed, self-circling and zero-discharging system, and completely solves two worldwide problems - material shortage and serious pollution existing in pulping & papermaking industry.

Summary of the invention

[0013] The invention overcomes the technical shortcomings in the prior arts and provides a close-loop, self-cycling, zero-discharging, clean oxidizing pulping process and the preparation method thereof.

[0014] The clean pulping process and preparation method thereof of the invention are characterized in that the raw materials of the clean pulping process and the preparation method thereof are non-wood

or wood material and preparation of the pulp can be finished according to the processes mentioned below:

(A) Pretreatment of raw materials;

(B) Materials pretreated above are oxidizing dipped in the presence of active oxygen A and cellulose protectant consisting of metal ions and metal ion ligands;

(C) The oxidizing-dipped materials are ground sequentially by the active oxygen A and then active oxygen B;

(D) Concentrating and beating;

wherein, the active oxygen A is one or two selected from O_2 , H_2O_2 , and free radicals generated from O_2 or H_2O_2 ; the active oxygen B is one or more selected from O_3 , 1O_2 (singlet oxygen), $O_2^{\cdot-}/HOO^{\cdot}$ (superoxide anion radical), and free radicals generated therefrom in water in the presence of an organic solvent.

[0015] In accordance with the present invention, the organic solvent is, for example, DMSO or oxalic acids.

[0016] A pulp obtained by the above process is also provided.

[0017] In the clean pulping method described above, the non-wood materials such as full cotton stalk include one or the mixture of two or more selected from cellulose, hemicellulose, lignin of cotton bast, cotton stem, cotton stalk root and full cotton holocellulose, valvular cotton, cotton short linter, cotton dregs, and cotton seed. Said woods include broad-leaved wood and needle-leaved wood, such as white pine, Masson pine, oregano pine, aspen wood, fast-growing poplar, birch and so on.

[0018] In accordance with the invention, the metal ions are one or the mixture of two or more selected from Mg^{2+} , Fe^{2+} , Mn^{2+} , Cu^{2+} , Al^{3+} , Zn^{2+} , Si^{2+} . The metal ion ligands are one or the mixture of two or more selected from dimethyl dioxirane (DMD), diethylenetriamine pentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), sodium alkyl-sulfonate, and polyoxyethylene alkylether.

[0019] Amount of the metal ions in weight is between 1-1000ppm.

[0020] The oxidizing dipping treatment is carried out in an acidic condition having a pH of between 1-4, preferably, between 1.5-2.5.

[0021] The grinding treatment is carried out in an acidic condition having a pH of between 1-4, preferably, between 2.5-3.8.

[0022] The acidic condition can be obtained by use of the active oxygen of the invention (such as HOO^{\cdot}) and can also be obtained by the addition of pH regulator.

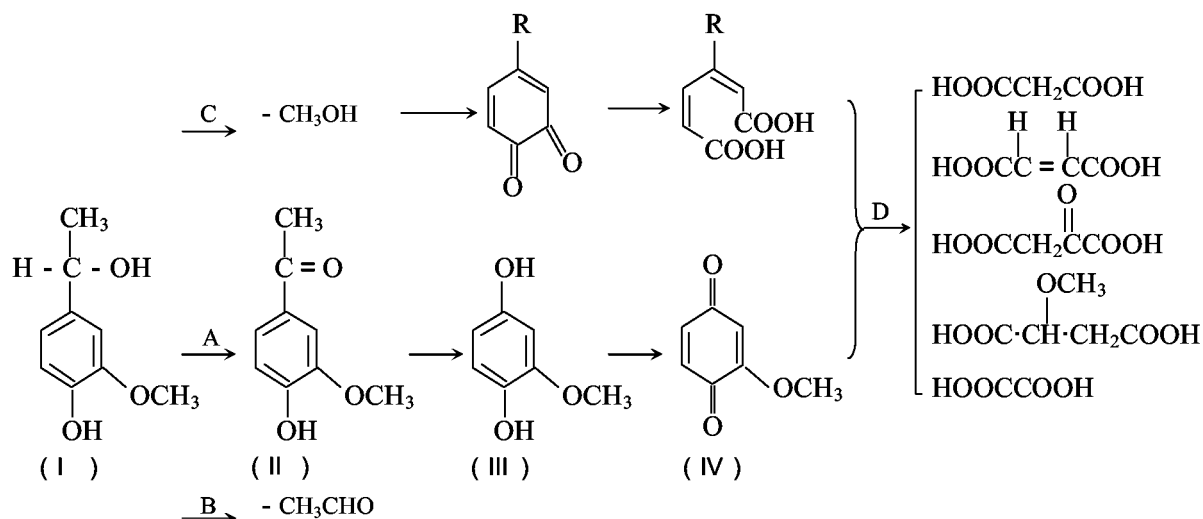
[0023] The concentration of active oxygen A in the materials being treated is 0.01-2.0wt%, and the concentration of active oxygen B in above materials is 0.1-50 μ mol/L.

[0024] A clean pulping method as stated above has the following features and advantages: (A) The active oxygen is dropped into a disc refiner, in which heat energy is generated from the rotation of the disc and is transferred into the materials for reaction, thus the cellulose is separated from the intercellular space; (B) With the combined effects of the active oxygen A and B, the chromophoric groups (α , β -aldehyde or ketone groups) in lignin are transformed into colorless groups (i.e., carboxylic acids or binary carboxylic acids); (C) Self-cycling: the raw materials pre-treated are delivered to the oxidation reactor. All water used in the process is divided into two parts to be cycled in the process: the first part is the water from the cleaning treatment of raw materials; after the centrifugal cleaning treatment, the resulting solid sediments are taken away and the resulting pulps are sent to the conventional beating process; water generated in the process is directed into a purification pool for cycling water in which a 0.1%-0.15% ozonizer (O_3 generator) is installed to decolor the water. The resulting water contains a very small amount of oxygen free radical and is then pumped into the cycling water system; the second part is the water from the oxidizing process, which water is cleaned with centrifugation and is then concentrated with a conventional decker. The pulp is sent to the pulp tank and then to a papermaking plant, and the water produced is filtrated and then sent to the water-purifying tank for self-cycling. The purified water is pumped into the material cleaning system, oxidizing-dipping system, oxygen grinding system and screening system for being recycled within the company.

[0025] The present method employs active oxygen free radicals generated by electron-reduction reaction of molecular oxygen in an ion reactor to transform and separate lignin, to change chromophoric groups in the intercellular space and to obtain paper pulp. The conventional pulping technologies that use harmful polluting chemicals such as acid, alkaline, chlorine, anthraquinone and so on are basically different with the method of the present invention. In the present invention, the cooking and bleaching process which generate severe pollution can be avoided, and the abundant annually grown fiber materials can be utilized in this process and water and energy can be saved. As a result, the cost of production can be reduced.

[0026] The active oxygen is added into the materials, and ground with a high-concentration defibrator which leads to a grinding heat reaction, so as to change lignin's chromophores in the intercellular space. Because the hydroxyl free radicals formed by the three oxygen atoms of molecular oxygen have a strong attack power and an intracellular nucleophilic attack power, and an electrophilic reaction occurs between the hydroxyl free radicals and lignin. The big π -bonds in the lignin structural elements, i.e., benzene ring and side chains, are broken, and then lignin is degraded and dissolved. The chromophores in lignin are transformed or decomposed into small molecules, thus forming colorless monocarboxylic acids or binary carboxylic acids.

[0027] The reactions are as follows:



[0028] The invention also includes the pulp made by the above process.

Process of the invention is described in detail as follows:

[0029] A clean oxidizing pulping process and the preparation method thereof, characterized in that the raw materials thereof are non-wood and wood materials and preparation of the pulp can be finished according to the following process:

(A) Pretreatment of raw materials;

(B) Materials pretreated above are oxidizing-dipped in the presence of active oxygen A and a cellulose protectant that is made of metal ions and metal ion ligands;

(C) The oxidizing-dipped materials are ground in turn by the active oxygen A and then active oxygen B;

(D) Concentrating and beating;

wherein, the active oxygen A is one or two selected from O_2 , H_2O_2 , and free radicals generated from O_2 , H_2O_2 ; the active oxygen B is one or more selected from O_3 , 1O_2 (singlet oxygen) $O_2^{\cdot -}/HOO^{\cdot}$ (superoxide anion free radical) and free radicals generated therefrom in water in the presence of an organic solvent.

[0030] Active oxygen can be obtained when molecular O_2 passes through an ion radiator in which an oxidation-reduction reaction can occur and when energy is provided, and at last water is formed. In the process that four electrons are accepted, one oxygen free radical will be generated when one electron is absorbed by O_2 . For instance, a superoxide

anion free radical is formed when O_2 is reduced by one electron and its equation is: $O_2 + e \rightarrow O_2^{\cdot -}/HOO^{\cdot}$;

hydrogen peroxide is formed when O_2 is reduced by two electrons and its equation is: $O_2 + 2e + 2H^+ \rightarrow H_2O_2$; hydroxy

free radicals are formed when O_2 is reduced by three electrons and free radicals are formed by reaction of Fe^{2+} and H_2O_2 , which are special free radicals for water treatment and their equations are: $O_2 + 3e + 3H^+ \rightarrow H_2O + \cdot OH$, $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$.

[0031] The metal ion(s) is/are one or the mixture of two or more selected from Mg^{2+} , Fe^{2+} , Mn^{2+} , Cu^{2+} , Al^{3+} , Zn^{2+} , and Si^{2+} . The metal ions are usually provided in the form of salts such as $FeSO_4$, $MgCO_3$, etc. The metal ion ligand(s) is/are one or the mixture of two or more selected from for example DMD, DTPA, EDTA, sodium alkylsulfonate, polyox-

yethylene alkylether. The metal ion, metal ion ligand, hyperoxide anion free radical ($O_2^{\cdot -}/HOO \cdot$) and H_2O_2 are

combined together in different compositions to form functional cellulose protection systems which can not only protect cellulose but also get rid of silicon.

[0032] Pretreatment usually includes removing impurity, shearing, fiberizing and, optionally, cleaning.

[0033] The oxidizing-dipping treatment is preferably carried out in acidic condition wherein pH is between 1-4, and preferably, between 1.5-2.5.

[0034] The grinding treatment is carried out in acidic condition wherein pH for example is between 1-4, and preferably, between 2.5-3.8.

[0035] The acidic condition can be obtained by the use of active oxygen of the invention (such as $HOO \cdot$) and also can be obtained by the addition of a pH regulator.

[0036] The metal ions are usually used in the form of a salt and the amount thereof is commonly between 1-1000ppm, preferably, between 10-100ppm by weight of metal ion.

[0037] In accordance with the present invention, "non-cooking" means that: the conventional cooking process can be omitted; instead, the active oxygen is dropped into the disc refiner, in which heat energy is generated through the rotation of the disc, and an energy transferring reaction occurs, then the cellulose is separated from the intercellular space.

[0038] In accordance with the present invention, no conventional bleaching process needed means that: the bleaching process can be omitted; instead, the combined effects of the active oxygen A and B are used in order to transform the chromophoric groups in the lignin into colorless groups, for example, to transform α , β -aldehyde or ketone groups into carboxylic acids or binary acids.

[0039] In accordance with a preferred embodiment of the invention, the process of the invention comprises:

a pretreatment system for the raw materials: this is a cooperation process. In this process, legumen and calyces of the raw materials are removed by a crushing engine, and then the raw materials are cut into pieces having a length of 5cm and a thickness of 1.5cm and a yield of 98%, broken into pluses by a rolling-type crushing engine, and then had dust and medulla removed by wind power while had impurity removed by a cleaner; wherein, water used in the cleaner is the water being cycled and full closed in the factory, containing minor active oxygen free radicals and minor cellulose protectant (commercially available), so no active oxygen is needed to be added in the pretreatment process. No drainage is discharged in the process of washing materials by the cycling water, which is different with the traditional acid washing and alkali washing process.

[0040] Oxidation reactor system (referring to Chinese patent application No.: 200310103895.3): the main function thereof is imbibition, softening and debonding of the materials; pH within the reactor is 1-4; active oxygen in the weak

acidic water generates superoxide anion radicals ($O_2^{\cdot -}/HOO \cdot$) which have strong penetrability and can penetrate

intercellular space directly to induce an oxidation-reduction reaction. An agitator is installed in the oxidation reactor and the agitator connects outer motor through the top of the reactor; the agitator is equipped with at least three layers of propellers, and its rotating speed can be controlled. Start the agitator and then in the reactor, positive ions are produced in the water by the electrodes. Materials are softened by the combined effects of pressure, temperature and shearing stress of the agitator. In the oxidation reactor, owing to the active oxygen, catenating layer, pectin, and polypentose are decomposed at the same time and decoloring reactions occur during the high speed agitation. With repeated experiments, the preferred reaction conditions are identified: pH in the reactor is 1.5-2.5 and a rotating speed of 40-80 r/min and 0.02-0.1% cellulose protectant that has been prepared. In 40-60 minutes, in the reactor, chromophores in the raw materials change from deep yellow to pale white, then materials are washed repeatedly and squeezed for removing the water.

[0041] Grinding system: preferred is disk grinder system that consists of two parts, one is model RL50S disc refiner or high consistency defibrator and the other is oxidation reactor. The process includes first refining and second refining. Active oxygen A is used in the first refining and active oxygen B is used in the second refining. The raw materials exported

from oxidizing-dipping system are fed to the refiner by a screw feeder homogeneously, then the materials are dipped by O_3 whose concentration is 1-15 μ mol/L, weight percentage of water is 30%, and pH is 2.5. Grinding rotating speed is 600-1200 r/min and the gap between the disks is 0.2-0.15mm. In first refining, active oxygen A whose weight percentage concentration is 0.1-1.5 is added in the shower water to mix and grind with materials. The materials are softened by grinding, and then the cellulose cladded in the intercellular space is separated. Main function of the grinding thermal reaction is to produce heat transfer reaction with confriction of refiner by mixing and grinding of active oxygen and materials. Chromophores of phenylpropane are oxidized by superoxide anion free radicals, molecular oxygen and hydrogen peroxide. With softening temperature differences among lignin, hemicellulose and cellulose, hydrophilic groups produced from oxidized exiguous fibers can be connected to the backbone of cellulose; as a result, yield is augmented by 8-12%. Key of the invention is the conditions of the process (such as sequence, pH, temperature, amount of active oxygen used, time, rotating speed, pressure and pulp concentration etc of the process as detailed in the present invention).

[0042] The process includes a first refining and a second refining. Slag sifted can be ground and screened repeatedly. After being transferred to the cleaner, edible citric acid aqueous solution whose weight percentage concentration is 0.12 and hydroxylamine whose weight percentage concentration is 0.01 are added and sprinkled to prevent dandy worm and oxidative stain. According to routine beating process, the pulp is beaten and the pulp thus obtained is the original pulp with a yield of 76% and an ISO whiteness of 52-65°. The process described above can be applied in the village and township enterprises in the area with abundant raw materials. The coarse pulp products can be supplied sufficiently to the consolidation pulp mills.

[0043] The raw pulps are fed to the refiner by a screw feeder homogeneously and continuously. In the first refining process O_2 (weight percentage concentration is 0.1) and/or H_2O_2 (weight percentage concentration is 1.5) prepared in advance are added dropwise to the pulp in a ratio of 1:0.12-0.15 (according to weight ratio) and mixed with the pulp in refiner at 60-80°C, pH2.5-3.8 and 12-15% consistency. The rotating speed of the refiner is 1300 r/min and the gap between the disks is 0.15-0.1 mm. The pulp whiteness can be 60-75°. In the second refining process O_3 (concentration

is 10 μ mol/L) and/or superoxide anion radicals ($O_2^{\cdot -}/HOO \cdot$) (concentration is 10 μ mol/L) and/or singlet oxygen (1O_2) (concentration is 10 μ mol/L) are added and mixed with the pulp at 80-100°C, pH2.5-3.8, 12-15% pulp consistency and 0.3-0.6 Mpa. The rotating speed of refiner disc is 1300 r/min and the gap between the disks is 0.15-0.1 mm. After 0.5-1 h, the ISO whiteness should reach 75-86°. The pulp is sent into the conventional screening process for fine screening. The refined pulp is sent into the cleaning process, condensed with a decker, beaten, and then sent into the storage process. When higher whiteness is required, the pulp can be processed again according to the process described above and pulp yield is 75%.

[0044] Compared with prior arts, the method of the invention has the following advantages: it is a preparation process of pulp which is fully closed, zero discharging, self-cycling, no acid needed, no alkali needed, no chlorine needed, no anthraquinone needed, no cooking needed, non-bleaching, and no pollution. The method has characteristics of saving energy, saving water and being a clean pulping method, and it solves pollution of papermaking completely, facilitates the re-use of agriculture and forest resources, and protects the biological environment. In accordance with the present invention, the fully closed, self-cycling, zero discharging refers to: raw materials are pretreated and then sent to the oxidizing dipping reaction system; all water in the process is divided into two parts to be self-cycled in the process; one part is the water from the process of centrifugal cleaning and beating, during which the solid sediments are taken away and the pulps are sent to the conventional beating process; water generated in the process is cycled into the purification pool. A 0.1%-0.15% ozonizer (O_3 generator) is installed in the purification pool to decolor the water. The water contains minor oxygen free radicals and is pumped into the cycling water system. The other part is the water from the following process: after the pulp is cleaned with centrifugal cleaner and then concentrated with a conventional decker, it is sent to the pulp tank and then to papermaking plant. The water produced is filtrated and placed in the water-purifying tank for self-cycling. The purified water is pumped into material cleaning system, oxidizing-dipping system, oxygen grinding system and screening system for being recycled within the company. No gas or black liquor is drained in the process. The solid residue discharged only occupies 12%-22% of the materials by weight. This process is pollution-free and the residue can be sent to bio-oxidation treatment tank for other uses.

Description of the drawings:

[0045] Figure.1 is the flow chart of this invention that is a fully-closed zero discharging and clean pulping process by oxidation.

Detailed description of this invention

[0046] Undermentioned examples are further description of the invention. These examples are only used to describe the invention, not to limit the scope of the invention.

EXAMPLE I

[0047] 100kg full cotton stalks were removed of legumen and calyces by a crushing engine and cut into pieces with a length of 5cm and a thickness of 1.5cm with a yield of 98%. Above materials were broken into plush by a roller-type crushing engine, had dust and medulla removed by wind power, impurity removed by screening, washed with cycling water before the materials were transported to the oxidation reactor (an auto agitator is installed in the reactor) by a screw feeder. The reaction conditions were 60°C, pH 2.5, a rotating speed of 60 r/min, with the addition of MgCO_3 0.02 kg and dimethyl-dioxirane (DMD) 0.01 kg. After 0.5h, a H_2O_2 solution with weight percentage concentration 0.2 was added. Then the rotating speed was increased to 80 r/min and temperature to 80°C. After 1 h, impregnating softness rate of the materials in the reactor was 98%. The materials changed from deep yellow to pale white and met with ISO whiteness 48-52° (hereinafter it is called whiteness or ISO whiteness for convenience). Above materials were washed repeatedly and dewatered to concentrate, giving a weight percentage concentration of water of 30%. A H_2O_2 solution was added into the material washed, and the weight percentage concentration of H_2O_2 in the material was 0.2. The material was fed to a refiner homogeneously to be ground. The rotating speed of refiner disc was 600-1200 r/min and the gap between the disks was 0.2-0.15mm. Slag sifted could be ground and screened repeatedly. After being transferred into the cleaner, an edible citric acid aqueous solution with a weight percentage concentration of 0.12 and hydroxylamine with a weight percentage concentration of 0.01 were added. According to routine beating process, the pulp was beaten, thereby obtaining an original pulp with a yield 76% and an ISO whiteness of 52-65°. The process described above can be applied in village and township enterprises in the area with abundant raw materials. The coarse pulp products can be supplied sufficiently to the consolidation pulp mills.

EXAMPLE II

[0048] 100kg raw materials from EXAMPLE I were fed to the refiner homogeneously and continuously by a screw feeder. In the first refining process H_2O_2 (weight percentage concentration was 1.5) prepared in advance were added to the pulp in a ratio of 1:0.12 (according to weight ratio) and mixed with pulp in the refiner at 60°C, pH3.8 and 12-15% consistency. The rotating speed of refiner was 1300 r/min and the gap between the disks was 0.15-0.1mm. The pulp whiteness was 65-75°. In the second refining process O_3 (concentration was 10 $\mu\text{mol/L}$) was added and mixed with pulp at 80°C, pH3.8, 12-15% pulp consistency and pressure 0.4Mpa. The rotating speed of refiner disc was 1300 r/min and the gap between the disks was 0.1mm. After 0.5-1 h, the ISO whiteness should reach 75-86°. The pulp was sent into the conventional screening process for fine screening. The refined pulp was sent into the cleaning process, condensed with a decker, beaten, and then sent into the storage process. When higher whiteness is required, the pulp can be processed again according to the process described above and pulp yield was 75%.

EXAMPLE III

[0049] Original pulps were obtained by the procedure as conducted in example I, except that MgSO_4 substituted for MgCO_3 at the same amount.

EXAMPLE IV

[0050] The same procedure as in example II was repeated, except that superoxide anion radicals ($\text{O}_2^{\cdot -}/\text{HOO}^{\cdot}$) whose concentration was 10 $\mu\text{mol/L}$ substituted for O_3 whose concentration was 10 $\mu\text{mol/L}$.

EXAMPLE V

[0051] 100kg poplar pieces were broken into plush by a roller-type crushing engine, had dust and impurity removed by wind power, washed by cycling water before the materials were transported to the oxidation reactor (an auto agitator was installed in the reactor) by a screw feeder. The reaction conditions were 60°C, pH2.5, rotating speed of 60 r/min and MgSO_4 0.015kg and dimethyl-dioxirane (DMD) 0.01 kg were added. After 0.5h, H_2O_2 solution with a weight per-

centage concentration of 0.2 was added. Then the rotating speed became 80 r/min and temperature was 100°C. After 1 h, impregnating expanding softness rate of the materials in the reactor was 98%. The color of the materials changed from deep yellow to pale white and ISO whiteness was 48-52°. Above materials were washed repeatedly and dewatered to concentrate, and weight percentage concentration of water was 30%. O₂ and H₂O₂ solution was added dropwise into the material, and weight percentage concentration of O₂ and H₂O₂ in the materials was 0.25. The materials were fed to a refiner homogeneously by a screw feeder so as to be ground. The rotating speed of refiner disc was 600-1200 r/min and the gap between the disks was 0.2-0.15mm. Slag sifted could be ground and screened repeatedly. After being treated in the cleaner, an edible citric acid aqueous solution whose weight percentage concentration was 0.12 and N, N-dialkyl hydroxylamine whose weight percentage concentration was 0.01 were added. According to routine beating process, the pulp was beaten, thereby obtaining an original pulp with a yield of 76% and ISO whiteness of 52-65°.

EXAMPLE VI

[0052] 100kg original pulp prepared in example V was fed to a refiner continuously and homogeneously by a screw feeder. In the first refining process, compound oxygen consisting of H₂O₂ (weight percentage concentration was 1.5) and O₂ (weight percentage concentration was 0.1) prepared in advance was added to the pulp in a ratio of 1:0.15 (according to the weight ratio) and mixed with pulp in the refiner at 60 °C, pH3.8 and 12-15% consistency. The rotating speed of refiner was 1300 r/min and the gap between the disks was 0.15-0.1mm. The pulp whiteness was 65-75°. In

the second refining process superoxide anion radicals ($\text{O}_2^{\cdot -}/\text{HOO}^{\cdot}$) (concentration 10umol/L) was added dropwise and mixed with the pulp at 80°C, pH3.8, 12-15 wt% pulp consistency and 0.4Mpa. The rotating speed of refiner disc was 1300 r/min and the gap was 0.1 mm. After 0.5-1 h, the ISO whiteness should reach 75-86°. The pulp was sent into the conventional screening process for fine screening. The refined pulp was sent into the cleaning process, condensed with a decker, beaten, and then sent into the storage process. When higher whiteness is required, the pulp can be processed again according to the process described above and the pulp yield was 75%.

EXAMPLE VII

[0053] Original pulp was obtained by the same procedure as conducted in example V, except that DTPA substituted for DMD at the same amount.

EXAMPLE VIII

[0054] The same procedure as conducted in example VI was carried out, except that singlet oxygen (¹O₂) whose concentration was 10umol/L and O₃ whose concentration was 10umol/L substituted for superoxide anion radicals

($\text{O}_2^{\cdot -}/\text{HOO}^{\cdot}$) whose concentration was 10umol/L.

[0055] In accordance with the present invention, there is provided a cooking-free, no bleaching needed, fully closed, self-cycling and active oxygen mixed refining process. The undesirable chemicals such as chloride, strong acid, strong alkaline are not employed. According to the market demands, enterprises can produce various types of pulps of middle or high quality.

The test results of the clean pulp produced by the oxidizing pulping process:

[0056] Pilot products, namely pulps of full cotton stalk, mulberry tree, poplar and the full cotton stalk fine pulp, were tested by Tianjin Science and Technology University. The results are shown in the testing report in detail (table 5). It is indicated that the oxidizing pulping technology can be applied to both wood and non-wood materials, and for example, full cotton stalk, an agriculture waste, can be utilized as raw materials for pulping.

[0057] A comparison between the testing report produced by Tianjin Science and Technology University on Nov 12, 2003 and national sulfite-bleaching pulping is listed in table 3.

Table 3

Index	GB Standard Of BSP	Cotton Stalk Pre-Screened Pulp	Cotton Stalk Screened Pulp	Mulberry Pre-Screened Pulp	Poplar Pre-Screened Pulp
Fiber length (mm)	0. 50	0. 51	0. 65	0. 47	0. 55
Degree of beating (°SR)	45	59	51.5	58	62
Basis weight (g/m ²)	58. 2	58.2	60.0	59.0	57.5
density (g/cm ³)	3.3	0.33	0. 32	0. 33	0. 32
Breaking length (Km)	3.2	3. 81	3.44	3.44	3.07
Tear index (mNm ² /g)	2.8	2.9	3.4	2. 9	2.5
Burst index (KPam ² /g)	1.5	1.9	1.5	1.7	1.4
Brightness (%ISO)	82.0	68.69	71.58	70. 87	75. 17
Opacity (%)	88.1	95.91	93.91	96. 05	94.07

Claims

1. A clean, fully-closed, zero discharging pulping process by oxidation and the preparation method thereof, **characterized in that** the raw materials thereof are non-wood or wood materials, and the process and the preparation method thereof comprises the following:

(A) pretreatment of the raw materials;

(B) the materials pretreated above are oxidizing-dipped in the presence of active oxygen A and a cellulose protectant consisting of metal ions and metal ion ligands;

(C) the materials treated by the oxidizing dipping are ground in turn by the active oxygen A and then active oxygen B;

(D) concentrating and beating;

wherein, the active oxygen A is one or two selected from O₂, H₂O₂, and the free radicals generated from O₂ and

H₂O₂; the active oxygen B is one or more selected from O₃, ¹O₂ (singlet oxygen), $\text{O}_2^{\cdot -}/\text{HOO}^{\cdot -}$ (superoxide anion

radical) and the free radicals generated from O₃, ¹O₂ and $\text{O}_2^{\cdot -}/\text{HOO}^{\cdot -}$ in water in the presence of an organic solvent.

2. The process according to claim 1, **characterized in that** the non-wood materials such as full cotton stalk include one or the mixture of two or more selected from cellulose, hemicellulose, lignin contained in cotton bast, cotton stem, cotton stalk root and full cotton holocellulose, valvular cotton, cotton short linter, cotton dregs, cottonseed; the wood materials include needle-leaved wood and broad-leaved wood such as white pine, Masson pine, oregano pine, aspen wood, fast-growing poplar, birch etceteras.

3. The process according to claim 1, **characterized in that** the metal ions are one or the mixture of two or more selected from Mg²⁺, Fe²⁺, Mn²⁺, Cu²⁺, Al³⁺, Zn²⁺, and Si²⁺; the metal ion ligands are one or the mixture of two or more selected from dimethyl dioxirane (DMD), diethylenetriamine pentaacetic acid (DTPA), ethylenediamine-tetraacetic acid (EDTA), sodium alkyl-sulfonate and polyoxyethylene alkylether.

4. The process according to claim 1, **characterized in that** the amount of the metal ions added is between 1-1000ppm by weight.
5. The process according to claim 1, **characterized in that** the oxidizing-dipping treatment is carried out in an acidic condition in which the pH is between 1-4.
6. The process according to claim 5, **characterized in that** the oxidizing dipping treatment is preferably carried out in an acidic condition in which the pH is between 1.5-2.5.
7. The process according to claim 1, **characterized in that** the grinding treatment is carried out in an acidic condition in which the pH is between 1-4,
8. The process according to claim 7, **characterized in that** the grinding treatment is preferably carried out in an acidic condition in which the pH is between 2.5-3.8.
9. The Process according to claim 1, **characterized in that** the concentration of active oxygen A in the materials being treated is 0.01-2.0wt%, the concentration of active oxygen B in the materials being treated is 0.1-50umol/L.
10. The process according to claim 1, **characterized in that** the process has the following features and advantages:
 - (A) during grinding process, the active oxygen is dropped into a disc refiner, in which heat energy is generated by the rotation of the disc, and the energy is transferred into the materials for reaction, and then the cellulose is separated from the intercellular space;
 - (B) with the combined effects of active oxygen A and B, the chromophoric groups, α , β -aldehyde or ketone groups, in the lignin are transformed into colorless groups, i.e, carboxylic acids or binary acids;
 - (C) self-cycling: raw materials are pretreated and then sent into the oxidation-dipping reaction system; all water in the process is divided into two parts to be self-cycled in the process: the first part is the water from the process of raw materials cleaning treatment, wherein it is purified by centrifugal cleaning and the solid sediments are taken away; the pulps are sent to the conventional beating process, and water generated in the process is cycled into a purification pool where a 0.1%-0.15% ozonizer (O_3 generator) is installed to decolor the water, and the resulting water contains minor oxygen free radicals and is pumped into the cycling water system; the second part is the water from the oxidizing process, which water is cleaned with centrifugation and then is concentrated with a common decker, the pulp is sent to the pulp tank and then to a papermaking plant, and the water produced is filtrated and sent to the water-purifying tank for self-cycling, the purified water is pumped into the material cleaning system, the oxidizing dipping system, the oxygen grinding system and the screening system for being recycled within the company.
11. The pulp obtained from a process according to any one of claims 1 to 10.

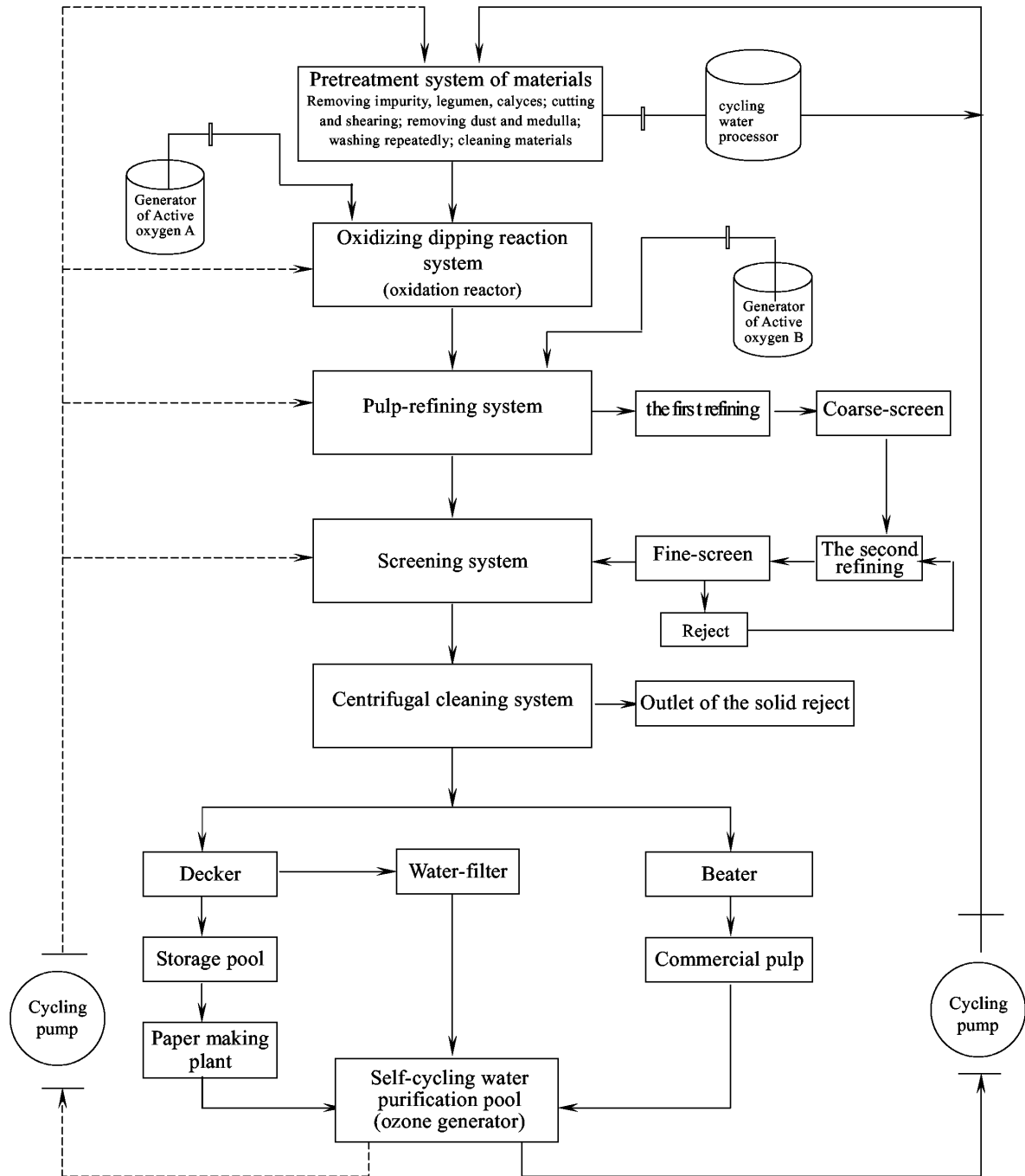


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN03/01121

A. CLASSIFICATION OF SUBJECT MATTER

Intcl⁷ D21C3/00, D21C9/147

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)

D21C3/00,3/02, 9/147, 9/153, 9/16,

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)

WPI, epodoc, PAJ, CNPAT, oxygen, ozone, superoxide anion, superoxide radical,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN1297085A, 30.May.2001(30.05.2001), the whole document	1-11
A	CN1142555A, 12.Fab.1997(12.02.1997), the whole document	1-11
A	CN1107530A, 30.Aug.1995(30.08.1995), the whole document	1-11
A	DE10126988A1, 12.Dec.2002(12.12.2002), English abstract	1-11
A	DE19612194A1, 02.Oct.1997(02.10.1997), English abstract	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search
17.sep.2004(17.09.04)

Date of mailing of the international search report

14 · OCT 2004 (14 · 10 · 2004)

Name and mailing address of the ISA/CN 100088
No.6 Xi Tu Cheng Road Haidian District Beijing, P.R.China

Authorized officer

Qi jianwei

Facsimile No. (86-10)62019451

Telephone No. (86-10)62084729



REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- FR 1999 [0010]
- CN 1212310 A [0011]
- CN 1371439 A [0011]
- CN 1407172 A [0011]
- CN 1198492 [0011]
- CN 1229155 [0011]
- CN 1458075 [0011]
- CN 200310103895 [0040]