METHODS FOR PRODUCING PULP AND TREATING BLACK LIQUOR

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Related U.S. Application Data

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Nov. 3, 2003 (GB)................................. 03 255 78.3
Aug. 7, 2001 (GB)................................. 01 192 37.6

A method is provided for treating black liquor particularly derived from non-wood pulp, by heating with an alkaline earth metal oxide in a toroidal fluidised bed reactor at a temperature of above 650° C. The method may be used alone or as part of a method of converting graminaceous raw material to pulp for paper or board, said method comprising (a) digesting said raw material with a white liquor based on sodium hydroxide and further comprising calcium hydroxide in an amount effective to substantially convert silica of said raw material to calcium silicate; (b) recovering pulp and black liquor substantially free of uncombined silica; (c) heating the black liquor in a fluidized bed reactor containing calcium oxide for catalysing conversion of organic content of said black liquor to gas and for providing recovered solids including sodium values of said white liquor and calcium oxide; and regenerating said white liquor using said recovered solids. The use of the above mentioned white liquor permits treatment of wheat straw, rice straw and other high-silica materials without resulting in a black liquor that is difficult to treat.
Fig. 1

Pulp for paper making

Rollers for raw material crushing and splitting

Contrary material extraction

Cellulosic raw materials

Black liquor effluent treatment

White Liquor

Multiple zone screw conveyor for raw material pulping
Feed hopper 103

Target rolls onto snail roller 105

Intermediate rollers 109

Intermediate roll opens for cleaning

Larger roll loads onto smaller roll

Knurled crushing rollers 107

Pinned rollers 113

Feeding shoe opens for cleaning

Treated straw hopper 115
Fig. 3

Pinned roll 120

Fibre 124

Perforated or woven belt 122
Fig. 4

- Cooking liquor
- Steam or oil into jacket
- Reversed flights
- Pulp out
- Some liquor squeezed out
- Raw material
METHODS FOR PRODUCING PULP AND TREATING BLACK LIQUOR

[0001] This application is a continuation-in-part of U.S. patent application Ser. No. 10/773,870, filed Feb. 6, 2004, which claims priority to PCT International Application No. PCT/GB2002/005641, filed Aug. 7, 2002, published as WO 2003/014467 on Feb. 20, 2003, which claims priority to GB 0119237.6, filed Aug. 7, 2001, to each of which priority is claimed, and each of which is incorporated by reference in its entirety herein. This application is also a continuation of PCT International Application No. PCT/GB2004/050023, filed Nov. 3, 2004, published as WO 2005/045126, which claims priority to UK Patent Application No. 03 25578.3, filed Nov. 3, 2003, to each of which priority is claimed, and each of which is incorporated by reference in its entirety herein.

FIELD OF THE INVENTION

[0002] The present invention relates to a method for producing pulp from graminaceous fibres and also to a method of treatment of black liquor that may be a by-product of said pulp production method or may have arisen otherwise e.g. Kraft black liquor or a mixture of soda black liquor with Kraft black liquor.

BACKGROUND TO THE INVENTION

The Kraft process

[0003] The principal component of wood is long straight translucent cellulose fibres based on chains of glucose molecules that make up about 42 wt % of softwoods and 45 wt % of hardwoods. Hemicelluloses form a further component of wood and are short, branched chains of glucose and other sugar molecules that are relatively soluble in water and are removed during the pulping process. The cellulose fibres are held together by lignin which is a three-dimensional phenolic polymer network that holds the cellulose fibres together and imparts rigidity. Lignin comprises about 28 wt % of softwood and about 20 wt % hardwood. It is selectively removed during chemical pulping and subsequent bleaching without significantly degrading the cellulose fibres. Extractives account for about 3 wt % of softwoods and about 5 wt % of hardwoods. They include plant hormones, resin and fatty acids.

[0004] The Kraft or sulphate process is preferred for the chemical pulping of wood because it can deal effectively with the resin component of many woods. It uses sodium hydroxide as the main cooking chemical and sodium sulphide as catalyst, and it gives stronger final pulp than the soda process, which employs sodium hydroxide alone. Anthraquinone is often used as an auxiliary catalyst in both the Kraft and soda processes. In the Kraft process, chips are cooked in a digester under heat and pressure with “white liquor” (in this case aqueous sodium hydroxide and sodium sulphide) to dissolve the lignin selectively. After 2 to 4 hours, the cooked mixture of pulp, spent pulping chemicals and wood waste is discharged from the digester. The resulting pulp is separated from a mixture of pulping chemicals and waste referred to as “black liquor”.

[0005] The treatment chemicals (sodium sulphide and sodium hydroxide) are then regenerated from the black liquor by a process whose main piece of equipment is a so-called Tomlinson furnace. Black liquor at about 65% dry solids content is sprayed into the furnace. During their descent, the black liquor droplets lose the remaining water by evaporation and the solids undergo pyrolysis to form a char bed at the bottom of the furnace. The char bed burns under reducing conditions at a temperature of 750⁰C-1050⁰C. and the recovered chemicals, mainly Na₂CO₃ and Na₂S, are drained from the furnace as a slurry which is dissolved in water to produce so-called green liquor, the precursor of the white liquor. The gases generated during pyrolysis and burning of the char are fully combusted at a higher location in the furnace. Flue gases must be thoroughly scrubbed to remove mercaptans that form under the process conditions. The furnace is provided with a suitable heat exchanger to recover heat from the hot combustion gases for steam and electricity generation.

[0006] Although useful recovery of chemicals and energy can be achieved in commercial operation, the use of a Tomlinson furnace presents a number of problems. For example, inadvertent contact between water or dilute black liquor and the inorganic smelt may result in an explosion. Also, high char bed temperatures lead to increasing emission of sodium salts and excessive fouling of the steam pipes in the upper part of the furnace. Furthermore, the technology currently used to treat black liquor effluent is, depending on local economic conditions, only viable on a scale of not less than 60,000 tonnes of pulp production per annum, which may be compared with the typical scale of a modern wood pulp mill which is over 360,000 tonnes of pulp production per annum. Treatment of straw and other graminaceous materials is, of course, on a much smaller scale inter alia because long-distance transport of bulky agricultural residues such as straw is uneconomic.

Fluidised Bed Recovery in the Kraft Process

[0007] To solve these problems, and also to reduce capital investment and increase the energy efficiency of the recovery operation, a number of Kraft recovery process have been described in which the smelt-water explosion hazard is eliminated and the emission of sodium salts reduced by maintaining the inorganic chemicals in solid rather than molten form.

[0008] This principle was disclosed in U.S. Pat. No. 3,309,262 (Copeland et al) which discloses a process for treating black liquor in a reaction vessel containing a fluidized bed of solid particles consisting substantially entirely of residual inorganic materials derived from the black liquor. The process comprises:

(a) concentrating the black liquor by evaporation to a solids content of 20-45 wt %, said liquor having a combustible content sufficient to support autogenous combustion;

(b) spraying the concentrated black liquor into free space above the bed so that substantial evaporation is achieved within said free space, and the remaining further concentrated atomised black liquor flows into the fluidised bed;

(c) maintaining fluidity of the bed by introducing at a speed of 30-150 cm/sec (1-5 ft/sec) oxygen-containing fluidizing gas in an amount sufficient to effect complete elimination of organic material as off-gas by substantially total autogenous combustion within the fluidised bed;
(d) maintaining the bed at a non-smelting temperature below the eutectic temperature of the residual chemical mixture within the bed but in a temperature range of about 540-982°C to form gaseous combustion products above the bed and agglomerates within the bed from the residual inorganic materials of the black liquor that are of sufficient weight to prevent their entrainment in the fluidizing gas;

(e) discharging the agglomerates from the fluidized bed; and

(f) discharging the off-gas from above the bed.

For sodium-based waste liquor the maximum recommended bed temperature is 760°C. (although the inventors are aware that this value was exceeded in practical operation). Introduction of the black liquor as a mixture of coarse and fine droplets is recommended in order to combine rapid evaporation of water, an efficient scrubbing action that reduces dust loading, and promotion and control of agglomeration of the bed particles. Oxidising conditions within the reactor are maintained to prevent the formation of hydrogen sulphide gas, and conversion of organic material into combustible gas is not disclosed. The end products are Na₂CO₃ and Na₂SO₃ which have to be subjected to recastification to regenerate white liquor. Although it has been reported in the patent literature that there have been attempts to commercialise the Copeland process, the inventors are aware that it is prone to severe bed agglomeration, especially when treating black liquor of relatively low caloric value from the cooking of straw, and that the process has since fallen into disuse for lack of technical and commercial viability. The experience of the inventors is that simple fluidized beds of the kind disclosed by Copeland are subject to unacceptable agglomeration, which makes operation impractical for anything beyond a short start-up period.

U.S. Pat. No. 3,523,864 (Osterman) discloses a recovery process for Kraft black liquor based on a reaction vessel having lower, intermediate and upper fluidized beds disposed one above another and each formed by pellets of CaO. The lower bed operates at 704-760°C (1300-1400°F) and contains solid reaction products in which Na₂SO₃ becomes reduced to Na₂S. The intermediate bed is at 648-704°C (1200-1300°F) and is fed with black liquor and preheated air in an amount of about 30% of that required for complete combustion to produce Na₂CO₃ and Na₂SO₄ which become deposited on the surface of the CaO pellets together with combustion gases and organics. The upper bed receives recycled CaCO₃ which becomes calcined to regenerate CaO and provide the material for the fluidised beds which descends progressively from upper to lower beds. Overhead combustion gases are partly recycled as fluidising gas and after cyclone treatment are partly fed to a steam generator. Again all three beds are of the same bubbling type, and the intermediate bed is subject to unacceptable agglomeration for the reasons already given.

There are two further reasons for the absence of commercial utilization of these low-temperature fluidized bed processes: firstly the relatively high temperature required for fast and complete conversion of Na₂SO₄ to Na₂S and secondly the ease of formation of H₂S when Na₂S is contacted with combustion gases below the melting point of the inorganic salts. So, while high temperatures favour the reduction, the above alternative processes require a relatively low temperature just below the melting point of the inorganic salt mixture. The consequence is that in fluid bed processes operating in the reducing mode, most of the Na₂S formed is rapidly converted to H₂S (and some COS) according to the overall reaction

$$\text{Na}_2\text{S} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{S}$$

resulting in a low recovery of solid Na₂S.

For the sake of completeness, there should be mentioned U.S. Pat. No. 4,011,129 (Tomlinson) which discloses a method for increasing the chemical recovery capacity of a Kraft recovery furnace by injecting solid pellets of sodium sulphate and sodium carbonate directly onto the char bed in the reducing zone of the furnace while maintaining the temperature and reducing atmosphere in that zone, whereby forming a smelt containing sodium sulphide and sodium carbonate from the injected pellets. These pellets may be produced from a further quantity of black liquor in an auxiliary incinerator such as a fluid bed combustion unit, which permits recovery capacity to be increased without needing the construction of a further recovery furnace.

Production of Non-Wood Cellulosic Pulp

The use of agricultural residues from graminaceous annual crops could provide a solution to many problems of concern to the pulp and paper industry including fibre supply, farmers’ concerns over the cost and availability of disposal alternatives, and consumer concerns over limited forest resources.

Broadly defined, graminaceous crop residues are the materials left over after annual agricultural crops have been harvested for their primary or intended purpose. They include cereal straws, such as wheat, rice, barley and oats; seed grass straws such as flax and rye; the crushed stalks of sugar cane known as bagasse; sorghum and corn stalks; and other agricultural residues e.g. cotton linters, the short fibres adhering to cotton seed after cotton ginning: In countries where there is little or no supply of wood, pulp from straw and bagasse is being used in high proportions for papermaking—up to 90% for high quality printing and writing paper. For example, in China, over 85% of papermaking pulp has been reported to come from non-wood raw materials, predominantly straw. In India, approximately 55% of papermaking pulp has been reported to come from non-wood sources with about half from agricultural-residues. As legislation increasingly prohibits the burning of agricultural wastes, there is new incentive to develop alternative uses for this resource. With proper soil management, farmers can supply small scale pulping mills with a continuous source of fibre while sustaining crop production.

Agricultural residues such as wheat and rice straw contain cellulose and can be a good raw material for papermaking. As previously mentioned, these raw materials are bulky, so that transportation costs and logistics mean that they are best pulped locally and therefore on a relatively small scale of around 10-100 tonnes of pulp production per day. Pulp mills generate black liquor effluent that if discharged to watercourses causes severe pollution. Lack of economically viable technology to deal with black liquor effluent under 60,000 tonnes per annum of production has meant that many existing small pulp mills have been forced to close to stop pollution of watercourses. This lack of suitable technology has also prevented the establishment of new small pulp mills, in particular new mills that might have
used agricultural residues. The subsequent lack of demand for small pulp mills has meant that little research and development of small pulp mill technology has been carried out. Consequently small pulp mill technology and straw pulping in particular has not advanced as far as large-scale wood pulping technology.

[0022] Straw can be pulped by chemical processes and by a combination mechanical and chemical process (chemo-mechanical pulping). For the cooking of non-wood raw material sodium hydroxide alone is recommended as the active chemical because most non-wood fibre does not contain sticky resins and the sodium sulphide catalyst is unnecessary. For this reason the major part of chemical pulp production from this class of raw materials is performed with a process called the soda process in which raw material is heated together with a highly alkaline cooking liquor containing sodium hydroxide to a temperature of 140-170°C. under pressure. Under these conditions, the main portion of lignin dissolves. Sodium hydroxide can be recovered from the resulting black liquor and organic substances in the black liquor can be used as fuel for energy generation. Contrary to the Kraft process, in which recovery requires reduction of sulphate to sulphide, black liquor from the soda process can be burnt even under highly oxidising conditions. Chemical recovery therefore involves evaporating the black liquor to a suitable content of dry matter and burning the evaporated liquor by means of excess oxygen. The inorganic combustion residue, consisting mainly of sodium carbonate, is dissolved in water and re-carbonised with burnt lime to regenerate sodium hydroxide, which is recycled. In a variant, slaked lime Ca(OH)₂ has been used in admixture with NaOH as active chemicals in white liquor because it also serves as a digesting agent and is of lower cost. However, a process for recycling NaOH/Ca(OH)₂ black liquors has not been described and such black liquors have in the past merely been discharged untreated.

Silica in Pulp from Graminaceous Starting Materials

[0023] The relatively high content of silica in straw and other non-wood cellulosic agricultural products presents difficulties for chemical recovery. Wheat straw contains 4-10 w% silica as small crystals embedded in the straw. Rice straw has an even higher silica content, 9-14 wt%. Other cereals such as barley, oat and rye straw have 1-6 wt% silica. Wood on the other hand has a silica content of less than 1 wt%. In the soda process as applied to straw pulping, most of the silica in the straw reacts with the sodium hydroxide to form water-soluble sodium silicate, which remains in the black liquor in addition to lignin and other organic compounds. Black liquor of high silica content gives rise to scaling (coating equipment with a glass like substance) especially in an evaporative process. A modified wood-based recovery system may be used if the silica content of the cereal straw is less than 5-6 wt%, but at higher capital and operating costs. However, for products of higher silica content, especially for rice straw, there has been up to now no process that is technologically and commercially viable.

[0024] Our WO 03/014467 (the disclosure of which is incorporated herein by reference) discloses a method for treating raw elongate material suitable for use in a paper making plant comprising:

- extracting contrary material from the raw material;
- crushing the raw material from which contrary material has been removed to remove nodes;
- splitting the crushed raw material lengthways;
- supplying the split raw material to a co-rotating screw conveyor divided into a plurality of zones and processing said material in said conveyor to produce pulp and a black liquor effluent;
- supplying treatment material to at least one zone;
- controlling the temperature and/or pressure of at least one zone; and
- spraying concentrated black liquor into a processing vessel in the form of a fluidised bed reactor for treatment of said black liquor, said processing vessel being part of treatment material and energy recovery means. The alkali supplied to the co-rotating screw conveyor to bring about pulping may include sodium hydroxide and additionally calcium hydroxide, which has the effect of precipitating silica onto the cellulosic fibres and preventing silica from entering the black liquor as calcium silicate.

[0032] WO 03/014467 further describes a process for treating black liquor in which black liquor effluent arising from the pulping process is collected in a digestion liquor storage tank and concentrated to 30-70% solids using a standard evaporator designed for concentration purposes. If the black liquor effluent has a solids concentration of 30% or above it may be treated directly in the processing vessel eliminating the evaporation step. The concentrated black liquor is moved to a reactor vessel at a temperature in excess of 90°C. using a pipe or an enclosed twin-screw transport system. The enclosed transport system is used to minimise the loss of organic components through vapourisation. A temperature in excess of 90°C. is required to decrease the viscosity of the black liquor so that it will transport without resistance. The black liquor is treated in a toroidal fluidised bed reactor vessel. Although a limit of 650°C. is specified for the upper temperature of the fluidised bed, in practice a maximum temperature of 610°C. has only ever been used. This is because at temperatures above 600°C., volatilisation of the inorganic alkali metal species present in the black liquor (e.g. Na and K) has been demonstrated to occur in other processes. When these species are in the vapour phase, additional process equipment is required to recover them at increased overall cost.

SUMMARY OF THE INVENTION

[0033] The advantage of a higher reaction temperature is the enhanced rate of reaction for black liquor processing and hence throughput may be increased, whilst maintaining output quality. We have now discovered that a temperature of above 650°C. can be used in the above mentioned black liquor recovery process. Recent experiments have shown that the loss of inorganic species from the black liquor when heated to between 650 and 700°C. or even 725°C. in the fluidised bed, was minimal, i.e. the losses were not economically significant, and hence no additional equipment was required to ensure their recovery.

[0034] According to the invention there is provided a method for treating black liquor, which comprises heating the black liquor at a temperature above 650°C. in a reactor containing an alkaline earth metal oxide, e.g. calcium oxide.
In the reactor the black liquor may react with the alkaline earth metal oxide to form a mixture of sodium hydroxide and sodium carbonate and alkaline earth metal carbonate and a volatile gas and liquid component which contains a combustible component and can be used as a fuel as in conventional treatment processes, e.g., a boiler.

In an alternative aspect, the invention provides a method of treating graminaceous materials which reduces or overcomes the problems associated with a high silica content in the resulting black liquor.

The invention further provides a method of converting graminaceous raw material to pulp for paper or board, said method comprising:

- digesting said raw material with a white liquor based on sodium hydroxide and further comprising calcium hydroxide in an amount effective to substantially convert silica of said raw material to calcium silicate;
- recovering pulp and black liquor substantially free of soluble silicate;
- heating the black liquor in a fluidized bed reactor containing calcium oxide for catalysing conversion of organic content of said black liquor to gas and for providing recovered solids including sodium values of said white liquor and calcium oxide; and
- regenerating said white liquor using said recovered solids.

Under some conditions, there is a risk that significant quantities of silicate may pass into black liquor streams during the pulp washing process. However, the inclusion of calcium hydroxide in alkali liquor used for pulping causes the silicate to pass into the black liquor as calcium silicate in preference to, or to the substantial exclusion of, sodium silicate. Calcium silicate is significantly less likely than sodium silicate to give rise to downstream processing problems. In a further aspect, the invention relates to the use of calcium hydroxide as an additive in the soda process digestion of a graminaceous starting material to form pulp for inhibiting scaling during black liquor concentration and recovery when processing black liquor at least partly from pulp washing.

DESCRIPTION OF THE DRAWINGS

The invention will now be described in greater detail, by way of example, with reference to the drawings in which:

- FIG. 1 is an overall block diagram of a process for making pulp from wheat straw according to the invention;
- FIG. 2 is a schematic view of a roller arrangement for use in a raw material pre-treatment process forming part of the pulp manufacturing process of FIG. 1;
- FIG. 3 is a schematic view of the construction of a self-cleaning pin roller that may be used in the roller arrangement of FIG. 2;
- FIG. 4 is a schematic view of a possible embodiment of a co-rotating twin screw conveyor that may be used for converting straw to pulp in the process of FIG. 1; and
- FIG. 5 is a block diagram of a preferred black liquor effluent treatment apparatus that may be used in the process of FIG. 1.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Overview of the Treatment of Wheat or Rice Straw

The present process will be described, by way of illustration with reference to the treatment of wheat straw, which is usually chopped before pulping and which contains nodes within the stem that usually remain intact if straw is chopped before pulping. This is a serious drawback in the production of quality paper pulp with the resulting poor quality paper being produced. A method is therefore preferably employed which crushes the nodes, opens out the straw stem lengthways in a gentle fashion and feeds the raw material into a digester in a positive, metered and continuous process. The straw to be treated passes from a delivery conveyor 9 to a straw pre-treatment station 10 where the stems are crushed between rollers, contrary material is extracted, and the stems are split longitudinally. The conditioned straw is then supplied to a digesting or pulping station 12 where it is subjected to mechanical work in the presence of aqueous alkali (white liquor) whilst subject to elevated temperatures and pressures. The resulting black liquor is then passed to an effluent treatment station 14 where it is heat treated to provide solids that can form a so-called green liquor. The liquor in turn is contacted with lime derived from a CaCO₃ feed and regenerated to white liquor for recycling to the pulping station 12. Off-gas recovered from heat-treating the black liquor can be used for generating steam and for process heat. A solids bleed of CaCO₃ sludge is removed to avoid excessive build-up of trace metals in the white liquor.

Pre-Treatment

Where straw is the raw material from which pulp is to be made, it may take the form of chopped straw, straw that has been subjected to a longitudinal splitting or shredding operation, or straw that has been both longitudinally split and/or shredded and chopped.

Referring now to FIG. 2, according to a preferred pre-treatment method, after the bales of straw have been opened, the straw is passed along a conveyor belt 101 where dust, heavy items such as stones and other contraries such as plastic string are removed. The straw is then passed into a feed hopper 103 which feeds the straw into an arrangement of knurled rollers 105 and 107 which crush the nodes in the straw stem and rollers with pins which open the straw stem out lengthways in a gentle fashion. Thus straw is fed between first and second counter-rotating knurled crushing rollers 105 and 107 to crush the straw nodes. The crushed material then passes through two counter-rotating intermediate rollers 109 and 111 that prevent any contrary materials from damaging the rollers below. The straw then passes through two more rollers 113 and 115, this time rotating in the same direction. These latter rollers are provided with pins that open and shred the straw lengthways and act in cooperation with a feed shoe.

The action of this system leaves the straw as shortened and opened out/shredded material without nodes. This will facilitate quicker chemical and steam penetration and so faster and more uniform pulping, whilst treating the fibres gently so preserving their length. This results in the production of an improved quality of pulp including a very significant reduction in visible “shiners” in the paper sheet.
due to dispersion of parenchyma cells, improved drainage, a higher tensile and tear strength, a higher pulp yield and a reduced demand for pulping chemicals.

[0053] The treated straw then drops from the pinned rollers 113 and 115 into feed hopper 117 leading to either a conveyor or blower system (not shown) that feeds the treated straw into a live bottom bin for buffer storage of the prepared material prior to pulping. The above discussed pinned and knurled or fluted roller opening and feeding system is specifically designed for straw but, with minor modifications, could be used for any other suitable raw materials including flax, hemp, bagasse and wood chips or sawdust.

[0054] The pinned rollers can also be constructed to be self-cleaning when used with longer fibered cellulosic raw materials such as hemp and flax. This is to prevent the material wrapping around the rollers and fouling the apparatus. A schematic of the functioning part of a pin roller is shown in FIG. 3. The pin roller 120 has an outer surface having a large number of radially extending pins 122. This is used with a matching perforated or woven belt 124 on which the material 126 being treated is carried. The pins 122 pick up the material 126 and as the belt 124 leaves the pins, it takes off the material keeping the pin roller 120 free from tangled fibres.

[0055] The above process has been tested and developed with straw, flax and hemp through pilot scale laboratory trials. Furthermore, the above-described pinning treatment for raw materials can be used with wood if the logs are flaked rather than chipped, as has been demonstrated using pinned wood wool instead of chips. This method of raw material preparation is particularly useful if the wood has a short fibre because the combination of flaking and pinning protects fibre length.

Digestion of Graminaceous and Other Cellulosic Starting Materials

[0056] Although chopped straw can be used as a feed, the preferred feed for the digestion stage of the present process is straw or other graminaceous plant stem material that has been longitudinally split and/or shredded. In such material the white liquor used for digestion makes easy contact with the graminaceous plant stem material and with any remaining node material, dissolving silica therein and digesting lignin and other alkali-sensitive materials.

[0057] For the cooking of non-wood raw material, sodium hydroxide alone is required as an active chemical, and for this reason the major part of chemical pulp production from these raw materials is performed with the process called the soda process. In that process the raw material is heated together with an alkaline cooking liquor containing sodium hydroxide to a temperature in the range from 140 to 170°C. or in some instances up to 180°C under pressure. The cooking liquor should have a high alkali concentration. Under these conditions, the main portion of lignin will be dissolved from the raw material; however, also the main portion of any silicon in the raw material will react with the sodium hydroxide, forming water-soluble sodium silicate. Thus the black liquor produced in cooking will contain silicate ions in addition to lignin and other organic compounds. The preferred white liquor used is therefore of the soda type (i.e. no sodium sulphide) and additionally contains calcium hydroxide in an amount effective to precipitate the silica. Either calcium hydroxide is present in the white liquor with which the graminaceous feed is treated, or calcium hydroxide is added shortly after the sodium hydroxide and in either case the amount of calcium hydroxide should be sufficient to precipitate silica onto the straw fibres as calcium silicate to reduce the soluble silicate content of the resulting black liquor. An effective amount of calcium hydroxide should be present to convert substantially all the silica or a desired portion thereof into insoluble silicate, much of which precipitates on the straw fibres, before extraction of black liquor from partially or completely digested straw is initiated.

[0058] The straw or other non-wood cellulosic material may be digested using a continuous digester, e.g. a single tube or multi-tube screw-fed digester, for example a Pandia digester available from Lenzing Technik GmbH & Co KG. The use of fast cooking of the plant fibre in a horizontal tube continuous digester with screw feeder is reviewed in Atchinson, J. E., Rapid Cooking Horizontal Tube Continuous Digester with Screw Feeder—Now the World Standard for Pulping Non-Wood Plant Fibres, 1990 Pulping Conference Proceedings. It is explained that this technology was developed initially for the pulping of bagasse, but is also applicable to other forms of non-wood plant material including wheat straw and rice straw. It is stated to permit a cooking time of only 10-15 minutes for bagasse, straw and most other non-wood plant fibres, in contrast, to earlier cooking methods using rotary batch digesters, which required cooking cycles of four hours or more. In the experience of the present inventors, this performance is over-stated, and it is impossible to produce a semi-chemical pulp in less than 20 minutes unless uneconomic quantities of cooking chemicals are used. The use of a screw feed permits the density of the feed material to be increased, and thereby the processing capacity of the digester, and also promotes continuous mixing of the white liquor and feed material. Again, to the inventors’ knowledge, the digester normally comprises 2, 3 or 4 series connected tubes each of diameter about 1 metre, so that the installation is of considerable size and capital cost.

[0059] Because of the rapid absorbancy of straw or bagasse when these materials are subjected to pressure and elevated temperature in a horizontal tube digester, especially after the pinning operation described above, pulping starts immediately and proceeds rapidly. The white liquor may be of the soda or Kraft type, and for straw or bagasse pulping typically 12-14 wt % NaOH or 6-7 wt % NaOH and 6-7 wt % Na2S are used based on the weight of the dry straw, with pulping temperatures of 170-180°C, pulping pressures of 7-9 bar and cooking times stated to be 10-15 minutes in order to produce a chemical pulp, and 3-5 minutes for a semi-chemical pulp. As explained above these figures are in the inventors’ experience not obtainable in practice.

[0060] A preferred pulping process for bagasse or straw (including rice straw) uses a horizontal tubular digester in which straw transport is by a conveyor based on a rotating and intermeshing double screw system. Such a digester can be made physically small for its processing capacity and consequently carries a lower capital cost than competing technologies. A significant advantage is that pulping can be conducted with low amounts of water, permitting black liquor to be produced at higher concentra-
tion and reducing or removing the need for subsequent black liquor evaporation. Shredded and/or chopped straw is continuously fed from storage into the barrel of the digester where white liquor and steam are injected through ports in the barrel or instead of steam injection electrical heating external to the barrel is provided. As the intermeshing twin screws rotate, the straw and black liquor are intermixed and the straw is worked mechanically and digested. The twin screw used is co-rotating, which reduces the mechanical treatment given to the fibres and thus minimises fibre damage to the fibres. In a twin screw arrangement transport along the barrel is primarily by the intermeshing flights of the two screws, whereas in a single screw conveyor transport is because the material is trapped between the advancing screw flights and the static barrel wall. The single screw arrangement is therefore less efficient because of friction and it can give rise to slippage (pressure in the barrel causes the straw to slip between the screw and the barrel wall) and surging. The material in the twin screw digester barrel with co-rotating screws travels in a figure-of-eight shaped path and thus takes a longer route than if the screws were counter rotating which gives better mixing of the straw and black liquor. The state of the art in relation to twin screw digesters for making paper pulp is shown in U.S. Pat. No. 4,088,528 (Berger et al) and U.S. Pat. No. 4,214,947 (Berger), the disclosures of which are incorporated herein by reference. It will be noted that both of these references are concerned with the treatment of wood chips rather than graminaceous material.

 Trials have confirmed that it is possible to produce using a single digester of the twin screw type to convert panned shredded straw of length about 25 mm into a chemical or semi-chemical pulp having a kappa number in the range 30-70 and useful e.g. for use in box or carton manufacture, corrugated packaging or the like. In a series of experiments, straw was fed into the inlet of a 40 mm diameter twin-screw digester, the pitch of the screw varying along its length to define five treatment zones of temperature ranging from 90° C. at the inlet to 165° C. in the penultimate zone. Alkali was added using a metering pump, with sufficient water to achieve the indicated liquid to solids digestion ratio. A temperature in the downstream cooking zones of the digester of not less than 165° C. was found preferable in order to achieve a well-disintegrated pulp. It was concluded that it is possible to achieve Kappa numbers in the low forties from a relatively short 40mm diameter twin screw, in less than one minute and with caustic additions below 10%, which represents a quality consistent with a semi-chemical pulp. In a full-scale machine it is envisaged that the cooking temperature would be 170° C. which is usual for making semi-chemical pulp using a continuous screw digester.

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</tr>
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<tbody>
<tr>
<td>Temperature</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>165</td>
</tr>
<tr>
<td>Screw Speed</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>50</td>
</tr>
<tr>
<td>Straw Feed Rate</td>
<td>6</td>
<td>3.75</td>
<td>6</td>
<td>6</td>
<td>6.3</td>
<td>6</td>
<td>3.75</td>
</tr>
<tr>
<td>Liquid to fibre ratio (to 1)</td>
<td>1.6</td>
<td>2.5</td>
<td>1.6</td>
<td>1.6</td>
<td>1.5</td>
<td>3.2</td>
<td>3.36</td>
</tr>
</tbody>
</table>

It is predicted that using a commercial scale twin-screw extruder, it may be possible to achieve fully digested chemical pulp suitable for printing or writing papers without an additional cooking stage with a retention time of e.g. about 1 minute and a cooking pressure of 7 bar. Alternatively the twin-screw extruder may be used to produce semi-chemical pulp in a first stage, which pulp may be converted into chemical pulp in a second cooking stage e.g. with 30 minutes additional cooking at a pressure of 7 bar before pulp de-watering.

An embodiment of a twin-screw co-rotating digester 131 appears in FIG. 4. Graminaceous raw material (straw, flax, hemp, bagasse), wood chips or any other cellulosic raw material from buffer storage can be pulped. To this end the raw material is drawn into the digester 131 in which the screw profiles are specially designed with two outer sections 133 and 134 having flights going in a first direction while in a middle section 135 the flight direction is reversed. The flights of the conveyor screws are manufactured from hardened steel with a deep cut flight to improve the size of the region where raw material is positively conveyed as explained above and are specially designed to minimize fibre damage. This particular design results in a reduced energy demand, which means that a smaller drive shaft and gearbox can be used, which also reduces capital cost. The design of the screw profile and the reduced drive shaft size also allows throughput of raw material to be increased by an anticipated 400% over conventional co-rotating twin screws.

As can be seen schematically in FIG. 4, one embodiment of the conveyor has a first zone 137 to which the raw material is fed through a feed hopper 139. The flights of the conveyor screws in zone 1 are designed to be as open as possible in order to accept the material into the unit. In a second zone 141 cooking liquor which is preferably a soda process white liquor not containing significant sulphite but containing Ca(OH)₂ can be added through an inlet 143 and steam can be introduced into the second zone of the digester barrel through inlet 145. The length of the region 141 and the dwell time of the raw material in that region vary depending upon the nature of the material, but are sufficient for a digestion of significant quantities of lignin located in regions of the starting material that are readily accessible to the pulping liquor (easy lignin) and dissolving other readily soluble material.

As explained above, it is desirable to convert silica present in straw or other graminaceous starting materials into insoluble silicate, much of which becomes precipitated onto the cellulosic fibres when pulping straw to prevent harmful amounts of silica from entering the black liquor effluent as soluble silicates which can give rise to scaling of evaporators or other parts of the downstream chemical
recovery system. For that purpose when pulping straw or other graminaceous material calcium hydroxide can be added in the second zone 141 at a rate of 4% to dry raw material (straw) with 8% sodium hydroxide. In general, there is used about one part by weight of calcium hydroxide for two parts by weight of sodium hydroxide. This method is applicable in any alkaline based pulping system and has the effect of re-precipitating sodium silicate onto the cellulosic fibres as calcium silicate some, most or substantially all of which can remain in situ on those fibres (depending upon the subsequent pulp treatment conditions) when they have separated as pulp and during subsequent washing, bleaching and conversion into paper. In a mixed alkali system in which both NaOH and Ca(OH)₂ are present, reaction to form insoluble CaSiO₃ is highly favoured over the competitive reaction to form soluble Na₂SiO₃, so that the silica is retained on the fibres as calcium silicate or enters the black liquor as insoluble calcium silicate. In consequence there is no significant difference as regards soluble silica content between the black liquor from graminaceous materials treated with NaOH/Ca(OH)₂ and the black liquor from wood pulping, which is amendable to treatment by known methods. The precipitated calcium silicate, once formed, is not prone to re-dissolve under the conditions encountered in subsequent pulp processing operations including bleaching, de-wathering and paper or board manufacture none of which employ low pH values (pH<4), and it simply provides an innocuous part of the ash content of the pulp, being chemically similar to Wollastonite which can be used as a filler in paper-making and also being similar to china clay which is a complex silicate. The only difference, so far as subsequent processing is concerned is that the pulp from graminaceous materials may have an ash content of e.g. 3-4% whereas the ash content of wood pulp is usually about 1%. It will be noted that the effluent treatment station 14 described below which gasifies the black liquor using a fluidized bed of CaO naturally produces a white liquor containing Ca(OH)₂ as well as regenerated NaOH, this black liquor both digesting the feed and precipitating calcium silicate on the cellulosic fibres so that it does not enter the black liquor in harmful quantities.

The partially digested raw material passes to a third zone 147 where the conveyor screws have a reversed flight region 135 which acts as a braking zone for the advancing raw material which forms a plug of material being processed, with a high pressure zone thus being generated upstream of the plug. In this zone the barrel wall has a perforated region 149 through which some of the cooking liquor becomes squeezed out. The action of the white liquor on the raw material is to rapidly solubilize all or much of the readily accessible lignin content of the raw material which dissolves with soluble hemicellulose and other dissolvable organic solids. In the third region a portion of the white liquor which may typically correspond to about half of the white liquor initially added exits the region 149 as a black liquor stream of high solids content, typically about 30 wt % solids. Removal of the easy lignin, soluble hemicellulose and other soluble organic materials in this black liquor stream means that these materials are no longer present to impede alkali attack on lignin remaining in the partly digested raw material in subsequent zones, assists the later stages of digestion, and also provides a solids-rich black liquor stream that contributes to recovery of a final combined black liquor stream of relatively high solids content.

A remainder of the barrel and conveyor screws define a fourth zone 151 and a fifth zone 132 leading to an outlet 153 for pulp. In Zone 4 temperature and pressure are increased as indicated so that digestion continues through residual white liquor on the pulp which also serves to lubricate the partly digested starting material as it progresses along the digester barrel. In Zone 5 temperature and pressure are reduced in preparation for the material leaving the twin-screw digester. The material travels through the twin-screw unit in between 2-5 minutes. The screw speed may be around 200 rpm. It will be appreciated that while the twin-screw digester shown is set up with four/five zones, any number of zones, suitably from 3 upwards can be used and for whatever treatment regime is required.

[0067] The digester is usually of modular construction which facilitates making changes to both screw and barrel configurations. This should be a cost-effective way to make use of one standard twin-screw unit to process many different types of cellulosic raw materials and/or to produce different grades of pulp simply by changing the screw and barrel configurations. Machine speeds of between 50-500 rpm may be used. A speed of 50-250 rpm has been used in practice. The speed needs to be adjusted for the raw material used and the pulp quality required. The twin-screw digester can be built in such a way that chemicals and liquids can be injected and liquids or steam can be vented or removed in each zone, which is a standard feature of twin-screw extruders. It has further been realized that a sophisticated gearbox and drive of the type conventionally used in twin-screw extruders is not necessary to suitably pulp fibres. A simple gearbox and drive can be used, reducing the capital cost and energy consumption. It is anticipated that the pulping system will consume less than half the energy of a conventional twin screw used for this purpose. In another embodiment of the digester (not shown), the feed zone into the conveyor screws is enlarged compared to the other zones to allow the raw material to be fed freely into said zone to increase the throughput of the conveyor. As the raw material moves forward into the treatment zone and the first and second pressure zones, the area within the co-rotating twin screw conveyor may be continually decreased which has the effect of continually increasing the pressure within the zones.

Using a co-rotating twin screw with a barrel size of 100 millimeters, the co-rotating intermeshing-twin screw extruder is set up with five zones as described below.

<table>
<thead>
<tr>
<th>Zone</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Straw intake</td>
<td>Treatment steam/alaki</td>
<td>Initial liquor recovery</td>
<td>Digestion</td>
<td>Digestion/discharge</td>
</tr>
<tr>
<td>T °C.</td>
<td>65</td>
<td>100</td>
<td>130</td>
<td>130</td>
<td>150</td>
</tr>
<tr>
<td>P (bar)</td>
<td>0</td>
<td>0</td>
<td>2-3</td>
<td>4-5</td>
<td>2-3</td>
</tr>
</tbody>
</table>

[0069] The pulp exiting from the twin screw may have approximately 50% moisture content and would be expected to have a Kappa Number of 30-40. This is an unbleached chemical pulp ready for bleaching using standard methods and suitable for printing and writing papers. A semi-chemical pulp with a higher kappa number suitable for use in fluted packaging can also be produced if required. The result
is a function of the rpm and the flight design or time spent in the twin-screw extruder together with the pressure, temperature and amount of pulping chemicals used. It is expected that kappa-numbers as low as 20 may be achievable using a single screw.

[0070] If production of a full chemical pulp is not achieved in the twin-screw digester 131 as expected, it may then be necessary for the pulp to be further digested e.g. in a further twin-screw digester or in a single screw digester of the kind disclosed by Atchison above e.g. using steam at 1-2 bar pressure (120°) for a further 20-40 minutes, and optionally adding further white liquor. Atchison discloses the use of a two horizontal tube digesters disposed one above another with the discharge outlet of the upper digester feeding partly digested material into the inlet of the second digester. In practice, in the prior art, it has often been necessary to use three such digesters arranged in series. However, the twin-screw digester disclosed above produces significant breakdown of the graminaceous or other starting material, and it is expected that only a single further twin- or single-screw digester stage will be needed to achieve a chemical pulp ready for bleaching so that installation size and capital cost may be reduced. A Kappa Number of 14-20 may be achieved after this further digestion.

[0071] Pulp from the twin-screw digester or from a subsequent further digestion stage is then washed for further recovery of black liquor before further treatment e.g. bleaching in the case of a chemical pulp. Washing is normally a multi-stage operation in which e.g. the pulp is successively contacted with wash liquid and passed through a plurality of dewatering stages arranged in series e.g. 2-4 such stages with 3 stages being usual. Some of the calcium silicate on the fibres may become dispersed in the wash liquor, and at the end of the multi-stage washing operation under come conditions e.g. about 50% of the calcium silicate may become re-dispersed into the wash liquor. Re-dispersion of calcium silicate may be inhibited by incorporation of a flocculating agent e.g. polyacrylamide into the wash liquor. However, under the conditions used in evaporation of the black liquor, any re-dispersed calcium silicate is significantly less prone to form harmful deposits than sodium silicate. Furthermore, calcium silicate is relatively water-insoluble and high melting, wollastonite melting at 1540° C., well above the bed temperatures for fluidized bed gasification of black liquor and well above the melting temperature of sodium silicate. Under the process conditions contemplated herein, it is expected that any calcium silicate in the black liquor will remain as discrete particles, and will not either volatilise or promote agglomeration of the fluidized bed used in the recovery process.

[0072] Each dewatering stage may take place in a screw-type press in which an elongated rotating screw fits within a foraminous sleeve that in turn is contained within a housing forming means for collecting wash liquor that has passed through the sleeve, pulp being advanced longitudinally of the screen by the rotating screw and being subjected to a squeezing action e.g. with the cross-sectional area of the channel defined by the screw thread or the spacing between adjacent screw threads diminishing from the inlet end of the screen towards the outlet, so that the pulp collected becomes compressed and liquid is progressively squeezed from the pulp. U.S. Pat. No. 6,792,850, U.S. Pat. No. 6,383,728, U.S. Pat. No. 6,736,054 and U.S. Pat. No. 3,256,808 illustrate some of the common features of this type of press. Wash liquid normally progresses in the opposite sense to the pulp so that if there are first, second and third screw presses connected in series, water is supplied to a mixing tank for washing the pulp to be fed to the third screw press, recovered wash liquor from the third press is supplied to a further mixing tank for washing the pulp to be fed to the second screw press, and recovered wash liquor from the second screw press fed to a mixing tank for washing the chemical pulp supplied to the first screw press, recovered liquor from the first screw press which may by now have a solids concentration of above 10 wt % e.g. about 12-15 wt % providing a relatively concentrated black liquor stream which can be combined with the still more concentrated black liquor stream at 149 and passed for alkali recovery. Some, or even a major part of the silica that has become converted into calcium silicate will find its way into the black liquor. However, the calcium silicate will not tend to dissolve under the recovery process conditions employed and in contrast to sodium silicate which is soluble will give rise to no or reduced harmful glassy deposits when the black liquor is concentrated by evaporation. It will be appreciated that in-line mixers may be used instead of mixing tanks, and that other known ways of dewatering pulp may be used in place of screw presses. Screw presses are relatively small compared to drum washers that could also be used, and are preferable for the smaller-scale operations involved in pulping of graminaceous materials.

Black Liquor Recovery

[0073] The present invention provides a recovery process to recover organic and inorganic chemicals and energy from black liquor effluent arising from the pulping of cellulose raw materials to make paper. It is specifically intended to be used with the above described pulping process but could be used alone to treat black liquor from other pulping processes. It is designed to be economically viable at small throughputs.

[0074] Owing to the absence of sulphides, the black liquor may be treated to volatilise the organic component thereof in a fluidized bed reactor under oxidizing conditions in the presence of a stoichiometric amount of oxygen or oxygen-containing gas such as air. Preferably, however, the black liquor is gasified (partially oxidised) to a synthesis gas having as components inter alia CO2, CO, H2O, and H2 usually together with methane and, C2H2, components under pyrolyzing or partial oxidizing conditions in the presence of a sub-stoichiometric amount of oxygen or free-oxygen-containing gas. Such gas may be a mixture of steam and combustion gas from a natural gas boiler, or a mixture of steam and combustion gas from a boiler supplied with cleaned recycled synthesis gas supplemented with natural gas as required. The gases act as fluidising medium for the bed, and the bed material consists of or comprises CaO which catalyses the gasification process and also the gasification of any char which may form as by-product within the bed. In such a process, the amount of oxygen in the gas mixture supplied to the bed should be sufficient to support partial oxidation and maintain bed temperature, but insufficient to convert the sodium and/or calcium hydroxide content of the black liquor entirely to carbonate, it being believed possible to conduct the reaction so that at least some of the NaOH remains as such in the bed. Thus the oxygen content of the fluidizing gas may be <5% oxygen.
and usually about 1.5-2% oxygen, giving an oxygen content in the off-gas above the bed of <1%, typically about 0.8%, all by volume.

[0075] Thermal degradation of the organic matter in black liquor begins above 200°C producing water vapor, CO₂, CO, H₂, light hydrocarbons, tar and in the case of Kraft and other sulfur containing liquors, light sulfur compounds (e.g. mercaptans). By 600°C, devolatilisation is essentially complete with the char residue containing fixed carbon, some hydrogen and most of the inorganic matter. Char composition can vary widely and depends upon both processing conditions (e.g. temperature) and fuel characteristics. Straw black liquor has a lower calorific value than wood black liquor, which should be taken into account when designing the fluidized bed reactor.

[0076] A series of non-isothermal experiments was conducted using temperature ramp thermogravimetric analysis (TGA). This technique allows rapid measurement of the temperature decomposition profile of a material and the subsequent determination of its thermal decomposition kinetics. For the straw black liquor, heated under N₂ at a rate of 20°C/min, five separate peaks were identified: (a) 25 to 105°C loss of moisture, (b) 105 to 250°C main volatiles peak, (c) 300 to 350°C smaller volatiles peak, (d) 425 to 500°C smaller volatiles peak and (e) 650°C, devolatilisation of inorganic species (e.g. Na and K). It was not possible to identify which organic components of the liquor were associated with specific peaks from these tests although it is likely the three main organic components, lignin, hemicellulose and carboxylic acids can be attributed to the three main volatiles peaks. These tests also indicate that the operating temperature of the industrial reactor should preferably not exceed 750°C in order to allow the majority of pulping chemicals (i.e. Na and K) to be recovered in the preferred solid form, reaction temperatures of e.g. 675-725°C being preferred, e.g. 675-700°C.

[0077] Batch fluidized bed experiments using a conventional or bubbling fluidized bed of silica sand of 0.1 m internal diameter were conducted to determine typical off-gas compositions and yields of char, off-gas and tars from black liquor pyrolysis, gasification and combustion experiments. Bed mixing and agglomeration tendency was also investigated. Black liquor concentrated to 29% and 45% solids was fed to the bed operating at 500-700°C, with U/Uₘₐₙ=4 (i.e. vigorously fluidized), supplied with mixtures of N₂ and O₂. Analysis of the off-gas showed typical compositions of the main product gases ranged between 0-5% for H₂, 7-12.5% for CH₄, 7.5-15% for CO, 55-89% for CO₂ and 0-8% for C₂, species. Bed agglomeration severe in all cases despite the high U/Uₘₐₙ and typically resulted in the experiment being terminated in less than 20 minutes, due to loss of fluidization. Gas yields were typically very low (around 9% at 550°C, increasing to 25% at 700°C). Together the low gas yields and gas compositions (i.e. high [CO₂] and low [CO] and [H₂]) suggest that the steam reforming reactions of the char were not occurring as they should under gasifying conditions. This is most likely due to the poor gas-solid contact occurring in an agglomerated fluidized bed. The increase in gas yield with temperature is important however and suggests an industrial reactor (which is designed to have a significantly higher tolerance for bed agglomeration) should be run as close to the melting point of K and Na as possible in order to maximize the production of synthesis gas. For pyrolysis experiments (with N₂ only), when a condenser was added to the off-gas line, the yield of tar (the condensable fraction) was measured to be 30 and 38% at 550 and 700 °C respectively. Char yields were 45% at 550°C decreasing to 39% at 600°C and 31% at 700°C, again suggesting temperature is an important process variable.

[0078] A spouted fluidized bed differs from a bubbling fluidized bed in that it is designed with a central jet that forces material from the base of the bed along the central axis before it is allowed to settle back down along the walls of the vessel. The bed is typically conically shaped rather than cylindrical to assist with the bulk circulation movement. It may exhibit greater bed stability and fewer tendencies to agglomerate than a bubbling fluidized bed.

[0079] The reactor is preferably a toroidal fluidized bed reactor; such reactors are described in U.S. Pat. Nos. 4,479, 920 and 4,559,719 (the disclosures of which are incorporated herein by reference) and are available from Torftech Limited of Reading, UK (www.torftech.com). Such a reactor is intended to overcome the problems of conventional fluidised bed reactors as regards control of temperature and rate of heat transfer within the bed resulting from the random nature of lateral movement of the bed particles in a bed that remains essentially static and is fluidised by a vertical flow of gas/air mixture. Both a bubbling fluidized bed and a spouting fluidized bed suffer from these problems. In the experience of the inventors, agglomeration occurs when there are hot spots in the bed. A toroidal fluidised bed minimises this risk and the active CaO bed will also help.

[0080] The solution proposed by Torftech and which is followed according to a preferred aspect of the invention, as applied to the treatment of black liquor, comprises providing a reactor having a processing region provided with a mass of particulate material consisting of or containing calcium oxide;

[0081] supplying heated fluidizing gas to the processing region so as to generate a swirling flow of fluid within said processing region, the fluid of said swirling flow of fluid causing the particulate material to assume a compact band and circulate about an axis of said processing region in a turbulent manner, the fluidizing gas including oxygen for at least partially combusting organic material in the black liquor;

[0082] feeding the black liquor into said compact band of particulate material and treating the black liquor in said bed so as to gasify organic materials in said black liquor;

[0083] recovering organic material from said black liquor; and

[0084] recovering inorganic material from said black liquor as solids from said bed.

[0085] It is believed that each particle travels to and fro inside the processing region along the full periphery of the compact band so that uniform processing conditions may be obtained. The motions of the particles within the particulate mass are determined by the combined effects of the fluid flow, gravity, and the centrifugal forces created by the swirling of the fluid, and the result is a thorough and continuous mixing of these particles and matter to be processed, on the supply of such matter into the band of
particles. Consequently, a very efficient processing operation may be achieved using only a shallow band of particles. Furthermore, the process gas stream impacts on and minimizes the insulating microscopic gas layer around each particle. As a result, the heat and mass transfer rate is greater than in other types of reactor, which should permit faster and more effective processing.

Tests have been carried out using a semi-industrial scale reactor of the above toroidal fluidized bed type. Where the black liquor to be treated is converted into solids form, the solids were fed through a two-stage screw feeder (one dosing screw, one feeding screw). Where the black liquor to be treated was in the form of a liquid, it was fed using a centrifugal pump either through the top of the reactor or through a two-phase nozzle (supplied with Ar or N₂) directly above and perpendicular to the bed surface. The off-gas and some solid material exited through the top of the reactor and passed through a length of duct into a cyclone and venturi scrubber before being passed to an afterburner chamber operating at 850°C. Bed solids were removed from the bed through a central discharge orifice. Solid and gas samples were taken from different locations around the plant. The reactor chamber was of a high temperature ceramic (not strictly required for this work) and was of 400 mm at the base rising to 500 mm at the top and was of height 850 mm. The distributor through which fluidizing gas entered the reactor chamber from beneath the fluidized bed comprised a number of parallel plates aligned at an angle, between which plates the fluidizing gases passed. The free surface area of the distributor was 30%. The effect of the distributor was to impart a severe swirling motion within the bed, which caused high local gas velocities and high turbulence without blowing particles out of the top of the reactor. The nominal fluidizing velocity used for all experiments was 10 m/s, which adequately supported a calcium oxide bed of mean particle size 1.5 mm.

Two different processing modes were considered for black liquor treatment in these experiments: (a) preparation of a premix containing black liquor and calcium oxide in a specified ratio and (b) direct spraying of black liquor (and various solids contents) onto a resident bed of quicklime in the reactor. Operationally, feeding a dried solid to the toroidal fluidized bed is the simplest alternative, but there are engineering issues that prevent this from being preferred. The reaction product with CaO is a plastic mass with thermoplastic properties (even using a substantial excess of lime) that requires further heating to achieve complete dryness and then cooling to achieve solidification before it can be crushed and fed through a gas-tight seal (e.g. a screw feeder or rotary valve) into the reactor. This is expensive and inconvenient. Furthermore, equilibrium modeling shows that an excess of CaO prevents the formation of hydrocarbons (particularly CH₄) by reaction to form CaCO₃. The alternative is to pump the black liquor directly onto a resident bed of CaO (mixed with inert material; either silica sand or alumina) inside the gasifier using a conventional black liquor spray nozzle. Swelling of black liquor as it reaches 200°C is a difficulty at the semi-industrial scale, but is not expected to be a problem with the larger equipment used on the industrial scale.

The bed solids containing the inorganic components from the black liquor, as well as the calcium from the catalyst, exit the bed via a central discharge weir where they can be dissolved to give a mixture of Na⁺, Ca²⁺, CO₃²⁻ and (OH)⁻ ions in solution according to the equation:

\[ \text{CaO} + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{NaOH} + \text{CaCO}_3 \]

This solution is then treated as described above.

The processing temperature used in these experiments ranged between 550 and 725°C. In general an increase in temperature increased the rate of conversion of the black liquor to reaction products. The majority of the inorganic content of the black liquor could be recovered in solid form at higher temperatures than previously believed possible. Typical recoveries were in excess of 90% where experimental data was measured within 95% confidence limits.

The influence of temperature upon the off-gas quality was indiscernible. The black liquor solids concentration also did not have a discernible influence upon either sodium recovery or off-gas composition but as expected the off-gas contained more water when the more dilute liquors (16% solids) were processed. It is expected that the optimum solids content for feeding to the black liquor process will be dictated by upstream processing conditions and economic constraints, i.e. the solids content produced by the pulping process and an analysis of the cost of evaporating water in the toroidal fluidized bed reactor compared with doing so in advance in a standard multi-effect evaporator.

As regards oxygen concentration in the fluidizing gas, early experiments with 5-20% [O₂] in the produced off-gas mixtures of N₂, CO₂ and H₂O as expected under these oxidizing conditions. Inorganic species recovery, i.e. Na, Ca and K, was good. Bed and cyclone underflow samples ranged from 39-60 wt % Ca and 2.5-13 wt % Na. Experiments conducted with <2% [O₂] produced gas mixtures containing predominantly N₂, CO₂, H₂O and hydrocarbons, H₂ or CO being difficult to detect chromatographically as they were obscured by the nitrogen peak.

Equilibrium modeling has shown that CaO is important for the gasification reaction. It also prevents solid carbon from forming (i.e. char and tars) and forms complexes with sulfur (specifically CaS), although this may have been seen as very much a beneficial side reaction. It is preferably added in the preferred amount CaO:DS (dry solids) of 0.2:1 to 0.4:1, most preferably about 0.35:1. At a ratio of 1:2:1 it lowers the amount of hydrocarbons formed considerably by tying up carbon as CaCO₃.

Thus, in a preferred embodiment, black liquor of solids content 10-40% e.g. 15-30% may be supplied directly to a toroidal fluidized bed reactor containing either calcium oxide alone or calcium oxide and an inert material, and supplied with steam and combustion gas from a burner supplied with recycled synthesis gas from the reactor supplemented with natural gas as required. An evaporation plant and a calciner to recover CaO from CaCO₃ are desirable, and a small quantity (about 10%) of the CaCO₃ stream will need to go to waste to prevent build-up of heavy elements which are naturally drawn up form the soil by the plants. This material could however be sent for local reprocessing and used to make bricks or in cement works.

Referring to FIG. 5, a preferred embodiment of the effluent treatment process will now be described.

Black liquor effluent arising from the pulping process is collected in a digestion liquor storage tank 301 and
concentrated to 30-70% solids using a standard evaporator 302 designed for concentration purposes. If the black liquor effluent comes from the co-rotating twin-screw conveyor at a solids concentration of 30% or above it may be treated directly in the processing vessel eliminating the evaporation step. The concentrated black liquor is moved to a reactor vessel 304 at a temperature in excess of 90° C. using an enclosed twin-screw transport system 303. The enclosed transport system is used to minimize the loss of organic components through vaporization. A temperature in excess of 90° C. is required to decrease the viscosity of the black liquor so that it becomes easy to transport. The black liquor is treated in the reactor vessel 304 in either of two methods.

[0096] In a first method, the black liquor is introduced into a toroidal fluidized bed reactor 304 by spraying the concentrated liquor into the chamber of the reactor in which a bed of fluidized material is supported. The material may be an earth oxide such as lime at a ratio of 0.3:1 of lime to black liquor dry solids. The mean particle size of the earth oxide may be between 1 and 4 mm. As previously explained, the reactor may operate under stoichiometric or sub-stoichiometric conditions. In a second method, black liquor effluent is pre-mixed in the twin screw conveyor 303 with an earth oxide such as lime (CaO) in the ratio e.g. 0.3:1 lime to black liquor dry solids to convert the black liquor a granular friable material which may then be screw fed into a toroidal fluidized bed reactor 304. Again when the black liquor is converted to a dry solid before it is supplied to the bed, the reactor may operate under stoichiometric or sub-stoichiometric conditions. In a variation of both methods, the ratio of earth oxide, e.g. lime to black liquor dry solids may be in the range 0.2 to 1.3:1 lime to black liquor dry solids. The earth oxide may be supplied by a standard caline reactor 308. In both cases the chamber of the toroidal fluidized bed reactor 304 is maintained within the temperature range 300 to 750° C. and preferably 650-750° C. where the necessary chemical reaction takes place in the space of seconds. In a further possible embodiment of the process a portion of the solids within the toroidal fluidized bed reactor 304 may be recycled via the screw feeder 303 back to the reactor 304.

[0097] The black liquor is converted by a chemical reaction to:

[0098] (1) Sodium hydroxide and sodium carbonate and lime within the fluidized bed reactor 304. The bed will overflow through a central discharge point and the overflowing material is then dissolved in a dissolving tank 305 to recover sodium hydroxide as green liquor in the traditional manner known as re-causticisation. The green liquor is then filtered using a known filter 306 to form a calcium carbonate sludge and white liquor (containing sodium hydroxide and calcium hydroxide) for re-use in the pulping process. However, in a variation of the process, if the temperature is carefully controlled, re-causticisation can take place in the reactor. In this case, sodium carbonate is not formed and the sodium hydroxide can be recovered without the use of the dissolving tank (306).

[0099] (2) A gas and liquids with a combustible component which can be utilized for energy production. The gas is collected to power a boiler 300 that will produce energy and steam for use in the pulp mill process line. In a further possible embodiment of the process the gas containing combustible components may be recycled to the fluidized bed reactor to provide heat for the chemical recovery reaction.

[0100] The calcium carbonate sludge may be dried to remove some water and sent to a second caline reactor 308, which may be a toroidal fluidized bed reactor. This reactor may operate at a temperature of around 1100° C. where calcium carbonate CaCO₃ is converted back to calcium oxide CaO for re-use in the black liquor effluent chemical recovery process. Approximately 10% of the fluidized bed material generated may need to be removed from the process continuously in order to prevent the build up of heavy metals and other materials in the process. If required, black liquor effluent below 30% solids can also be processed using this method (and has been tested). However energy consumption is greater and so this is not preferred.

[0101] It will be appreciated that various changes may be made to the embodiment described above without departing from the invention. For example, the black liquor treated in the fluidized bed could be a Kraft liquor or a mixture of the soda/Ca(OH)₂ black liquor and Kraft liquor or black liquor from the soda/anthraquinone process.

1. A method for treating black liquor to produce inorganic material and a synthesis gas having as components CO₂, CO, H₂O, and H₂ together with methane and, C₂+ components, said process comprising:

- providing a reactor having a processing region provided with a mass of particulate material consisting of or containing an alkaline earth metal oxide;
- supplying heated fluidizing gas to the processing region so as to induce a swirling flow of the particulate material within said processing region, the particulate material to assuming a compact band and circulating about an axis of said processing region in a turbulent manner, the fluidizing gas including a sub-stoichiometric quantity of oxygen for partially oxidizing the organic material of the black liquor and for converting other organic material of the black liquor to said synthesis gas;
- feeding the black liquor into said compact band of said particulate material so that it is heated at a temperature of 650-725° C. and becomes gasified;
- recovering said synthesis gas as off-gas from said bed containing <1% by volume of oxygen; and
- recovering inorganic material from said black liquor as solids from said bed.

2. The method of claim 1, wherein the black liquor is from the pulping of a graminaceous material selected from straw of wheat, rice, barley, oats, flax, rye, bagasse, sorghum or corn.

3. The method of claim 2, wherein the black liquor is from a soda-type white liquor containing calcium hydroxide in an amount effective to convert harmful silica in said graminaceous material to calcium silicate.

4. The method of claim 1, wherein the black liquor comprises 15-30% solids.

5. The method of claim 1, which comprises heating the black liquor at 675-700° C.

6. The method of claim 1, wherein the particulate material consists of or contains calcium oxide of mean particle size
of the calcium oxide between 1 and 4 mm, the black liquor and calcium oxide being supplied to the fluidized bed so as to maintain a ratio of calcium oxide to dry solids of the black liquor of 0.2:1 to 0.4:1.

7. The method of claim 6, in which the black liquor is pre-mixed with calcium oxide to become a granular friable material and the granular friable material is then fed into the fluidised bed reactor.

8. The method of claim 7, in which sodium hydroxide and/or sodium carbonate and calcium hydroxide and/or calcium carbonate are produced within the fluidised bed reactor.

9. The method of claim 1, in which the black liquor is introduced into the fluidised bed reactor by spraying the concentrated liquor into the chamber of the reactor in which a bed of fluidised material is supported.

10. The method of claim 9, wherein the nominal fluidizing velocity of the gases supplied to said bed is >2 m/s.

11. The method of claim 1, in which the fluidised bed overflows through a central discharge point, overflowing material is then dissolved in a dissolving tank to recover sodium hydroxide as green liquor and the green liquor is filtered to make a calcium carbonate sludge and white liquor containing sodium hydroxide for re-use in the pulping process, substantially no sodium carbonate being formed.

12. A method of converting gramineaceous raw material to pulp for paper or board, said method comprising:

- digesting said raw material with a white liquor based on sodium hydroxide and further comprising calcium hydroxide in an amount effective to substantially convert silica of said raw material to calcium silicate;
- recovering pulp from said digestion step;
- recovering black liquor from said digestion step by washing said digested pulp and optionally also by recovering black liquor direct from said digestion step, said recovered black liquor being substantially free of soluble silicate;
- heating the black liquor in a fluidized bed reactor containing calcium oxide for catalysing conversion of organic content of said black liquor to gas and for providing recovered solids including sodium values of said white liquor and calcium oxide; and
- regenerating said white liquor using said recovered solids.

13. The method of claim 12, wherein said gramineaceous raw material is wheat straw, rice straw or bagasse.

14. The method of claim 12, wherein recovery of black liquor includes combining a black liquor stream from the digestion step with a black liquor stream from the pulp washing step, and the black liquor is concentrated by evaporation to a solids content of 20-40 wt % before heating in said fluidized bed reactor.

15. The method of claim 12, wherein the fluidizing gases contain at least stoichiometric quantities of free oxygen for completely oxidizing the organic material of the black liquor.

16. The method of claim 12, wherein the fluidizing gases contain a sub-stoichiometric quantity of oxygen for partially oxidizing the organic material of the black liquor and for converting other organic material of the black liquor to a combustible off-gas and further comprising supplying fluidizing gases and black liquor so as to produce an off-gas above said bed containing <1% oxygen.

17. The method of claim 12, comprising:

- providing a reactor having a processing region provided with a mass of particulate material consisting of or containing calcium oxide;
- supplying heated fluidizing gas to the processing region so as to generate a swirling flow of fluid within said processing region, the fluid of said swirling flow of fluid causing the particulate material to assume a compact band and circulate about an axis of said processing region in a turbulent manner, the fluidizing gas including oxygen for at least partially combusting organic material in the black liquor;
- feeding the black liquor into said compact band of particulate material and treating the black liquor in said bed so as to gasify organic materials in said black liquor;
- recovering organic material from said black liquor as off-gas from said bed; and
- recovering inorganic material from said black liquor as solids from said bed.

18. The method of claim 17, wherein the raw material supplied for digestion has been crushed to remove nodes therefrom and split lengthways, crushing being by means of a pair of counter rotating knurled rollers between which the raw material passes, and splitting being by means of a pair of counter rotating pinned rollers between which the crushed material passes.

19. Use of calcium hydroxide as an additive in the soda process digestion of a gramineaceous starting material to form pulp for inhibiting scaling during black liquor concentration and recovery when processing black liquor at least partly from pulp washing.

20. The use of claim 19, wherein the black liquor is partly from a digester and partly from pulp washing, silica in said black liquor in the form of calcium silicate to the substantial exclusion of sodium silicate, a flocculating agent is added during washing to inhibit dispersion of calcium silicate said flocculating agent being polyacrylamide.