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(54) Title: USE OF CARBON DIOXIDE GENERATED IN MANUFACTURING SYNTHETIC HYDROCARBON CHAINS

(57) Abstract: The invention relates to the use of a carbon dioxide stream generated in oxygen gasification of organic matter for carbonating calcium from a liquid containing calcium ions. The invention also relates to a manufacturing process of paper or board, wherein organic matter is gasified with oxygen in order to carbonate the calcium, the produced carbon dioxide stream is reacted with a liquid containing calcium ions and the carbonated calcium is added to the pulp during the papermaking process as a filler or onto finished paper as a coating.

Use of Carbon Dioxide Generated in Manufacturing Synthetic Hydrocarbon Chains

Technical Field

The invention relates to the use of a carbon dioxide stream generated in oxygen gasification. More specifically, the invention relates to the use of the carbon dioxide stream generated in the oxygen gasification of organic matter for carbonating calcium from calcium-rich liquid, as well as to a papermaking process, in which the calcium carbonate precipitated by using the carbon dioxide stream generated in oxygen gasification is added to paper.

Background of the Technique

The limited supply of fossil fuels, as well as the emissions resulting from their use, have lead into added pressure for developing production methods of more environmentally-friendly fuels. The use of biomass as an energy source and especially in the production of fuels is one attempt towards diminishing environmental load in the the future.

In regard to energy production, biomass mainly refers to various types of organic waste, i.e. waste that is of biological origin, for instance wood, agricultural waste, municipal waste, waste land or plants. The process of burning biomass releases energy, referred to as bioenergy, but biomass may also be treated by other methods in order to achieve improved efficiency and smaller emissions.

Lately, attempts have also been made to use biomass in the production of liquid fuels, in which case the biomass is first gasified, and the obtained gas is transformed into biofuel. This multi-step process is referred to as Biomass to Liquid (BLT).

Gasification is an exothermic process, wherein a carbon-containing material, such as biomass, is converted into carbon monoxide and hydrogen. Three reactions occur in the gasifier, namely pyrolysis, in which volatiles are released and charcoal is produced, the combustion process, in which the volatile substances and some of the charcoal react with oxygen to form carbon dioxide and carbon monoxide, and the actual gasification reaction,

in which charcoal reacts with carbon dioxide and steam forming carbon monoxide and hydrogen. Both pyrolysis and combustion are extremely rapid reactions.

In the presence of steam and oxygen, a synthesis gas mixture is formed in the gasifier in accordance with the following reactions:

$$C + H_2O \rightarrow CO + H_2 \quad (1)$$

$$C + 2\,H_2O \rightarrow CO_2 + 2\,H_2 \quad (2)$$

$$C + CO_2 \rightarrow 2\,CO \quad (3)$$

$$C + \tfrac{1}{2}\,O_2 \rightarrow CO \quad (4)$$

$$C + O_2 \rightarrow CO_2 \quad (5)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (6)$$

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O \quad (7)$$

The most common gasification techniques comprise co-current gasification, in which the fuel and air mainly flow into the same direction, counter-current gasification, in which the air is supplied from below and the fuel from the top of the reactor, fluidized bed reactor and entrained flow gasifier.

Integrated Gasification Combined Cycles (IGCC) developed for industrial purposes are based on these different gasification methods (oxygen or air gasification, entrained flow, fluidized bed or fixed bed reactors) and different gas purification methods (chemical or physical purification, such as wet scrubbing or thermal purification).

The main components of the product or synthesis gas mixture formed as a result of the gasification are carbon monoxide and hydrogen. In addition to these, the mixture may as impurities contain for instance CO_2 (carbon dioxide), CH_4 (methane), H_2O (water), N_2 (nitrogen), H_2S (hydrogen sulphide), NH_3 (ammonia), HCl (hydrogen chloride), tar and small particles, such as ash and carbon black. This synthesis gas may also be referred to as woodgas, in case the fed biomass is wood.

Synthesis gas may be used as fuel as such, or the gas may be treated further in order to prepare gaseous or liquid fuels or chemicals by using different methods, such as Fischer-Tropsch fuel synthesis, methanol synthesis, or it may be used for hydrogen production by

water-gas exchange. In a combustion processes, flue gases need to be removed by purification, whereas in gasification the removable substances comprise product gas particles, alkali metals, nitrogen, tar, sulphur and chlorine. Gas purification may also comprise adding hydrogen to the synthesis gas in order to create a hydrogen-carbon monoxide ratio suitable for a Fischer-Tropsch process.

Various physical purification methods may be used for purifying synthesis gas mixtures, for instance Selexol® (UOP LLC), Rectisol® (Lurgi AG) or Purisol® (Lurgi AG), and/or chemical purification methods such as amine wash.

Rectisol® is a physical gas purification process, in which methanol is typically used as the organic solvent in a below-zero temperature. Rectisol® processes are preferably performed in high pressures, which usually exceed 30 bar.

Synthesis gas may be transformed into synthetic fuel by Fischer-Tropsch synthesis (FT-synthesis). FT-synthesis is a catalytic chemical reaction in which carbon monoxide and hydrogen are transformed into different liquid hydrocarbons. Before the actual FT-synthesis, the synthesis gas mixture needs to be purified. The H_2/CO molar ratio of the synthesis gas fed into the FT-reactor is preferably between 2.5:1 and 0.5:1, more preferably between 2.1:1 and 1.8:1, and most preferably about 2:1 or 1:1, depending on the catalyst used.

In FT-synthesis, synthesis gases CO and H_2 react exothermically, forming mainly aliphatic hydrocarbons. In addition to paraffins, smaller amounts of olefins, primary alcohols and water are formed. The hydrocarbon synthesis occurs according to the following reactions:

$$CO + 2\ H_2 \rightarrow -(CH_2)- + H_2O \quad (8)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (9)$$

$$2\ CO + H_2 \rightarrow -(CH_2)- + CO_2 \quad (10)$$

Cobalt or iron is used as the reaction catalyst. Of these two, cobalt results in a better conversion, and a cobalt catalyst also exhibits a longer life span. From the FT-reaction, a mixture of hydrocarbon compounds of different lengths is obtained, and this may be steered into the desired direction by selecting a suitable reactor and a catalyst and by

adjusting temperature, pressure and retention time. Typical reaction conditions range from 200°C to 350°C and from 15 bar to 40 bar. In higher temperatures, mainly short-chain compounds are synthesized, whereas in lower temperatures more long-chain hydrocarbons are formed. By-products, which have been separated from the end-product by distillation, may be supplied to the chemical industry to be used as raw materials. The end products of the FT-process contain no sulphur or aromates. Fuel produced by using this technology may be mixed with low-sulphur fossil fuels.

US 2007/0100003 A1 discloses a biomass gasification method, wherein carbon-rich material is pyrolyzed, after which the obtained bio oil and charcoal are treated further in a rotary entrained flow gasifier.

Pulp is produced from wood mainly in two different ways, by mechanical or chemical treatment. During chemical treatment, wood chip or non-wood material is treated with heat and chemicals such as lye, separating the fibres in the wood material from each other and dissolving lignin, the binding substance that keeps the fibres together. Alternatively, the wood may be mechanically kneaded. Friction transforms mechanical work into heat, which softens the lignin that binds the wood fibres together and opens the bindings between the fibres. As a result of this treatment, wood is made into a mass (a chemical or a mechanical mass), which is washed and most often bleached. If the mass preparation is integrated into a paper mill, the mass may be led directly from wash/bleaching into mass treatment in a paper machine. If this is not possible, the mass is dried and baled for later use. The mass may also be supplied to a paper mill which does not have its own mass production.

In a paper mill, mass is treated in several steps before it is fed into the headbox. Large particles such as splinters are removed from the mass, it is diluted by adding water and various additional substances are added thereto, for instance retention agents and fillers. The main advantages of added fillers comprise increased opacity, control of matt or bright finish, and diminished raw material costs. The fibre mass fed into the headbox contains more than 90 percent of water.

From the headbox, the fibre mass is fed onto a moving, water-permeable wire, and as water is removed, a continuous paper web is formed on the wire. Water is first removed from the paper web by sucking water trough the wire and then by using a wet press, after which the wire is finally transferred into a dryer section, where final drying is performed by using heated cylinders provided in the dryer section. The dried paper web is cut and wound into final products.

Various coatings and surface treatment agents may be added to the finished paper, which improve the paper characteristics, making it more suitable for its intended use.

The filler agents used in papermaking may comprise for instance pigments originating from rock material. Up to a third of the composition of a higher-quality paper may comprise minerals. Besides as fillers, minerals are in top-quality papers or boards used as special coating agents. The purpose of the use of minerals is to prevent ink from absorbing into the paper, whereby more precise letters are obtained. Another purpose of the minerals is to reflect light so that the print does not shine through the paper. By this way, a clear contrast may be created between ink and white paper. Minerals also slow down the breakdown of the paper, thus lengthening its life. Most commonly used minerals include kaolinite clay, calcium carbonate and talc.

Synthetic or precipitated calcium carbonate (PPC) is commonly prepared for the purposes of the paper industry in a so-called satellite mill in connection with the paper mill, by using the flue gas produced in the mill integrate as the carbon dioxide source and supplying the precipitated calcium carbonate that is suitable for use in papermaking directly into the process.

Calcium carbonate is produced from calcium oxide (CaO), i.e. burned lime or unslaked lime, which is obtained by heating quarried limestone, $CaCO_3$, in a lime kiln at a temperature of about 1,000°C. Calcium oxide is mixed with water, whereby a water suspension containing slaked lime, i.e. calcium hydroxide ($Ca(OH)_2$), is formed (called cream of lime). The obtained calcium hydroxide is carbonated by using pure carbon dioxide or for instance carbon dioxide obtained from flue gases or lime kiln exhaust gases, whereby calcium carbonate and water are obtained. In case the neutralization of the slaked

lime by carbon dioxide is incomplete, excess calcium hydroxide may lead to an overly high alkalinity.

Precipitated calcium carbonate may, if desired, also be prepared by adding the calcium ions (for instance in the form of calcium hydroxide) and the carbon dioxide directly into the papermaking process (*in-situ*). The precipitated calcium carbonate is typically prepared by a batch process.

The content of the above-mentioned patent application US 2007/0100003 A1 is herewith included in the present application in its entirety.

Brief Description of the Invention

The object of the invention is to utilize the carbon dioxide stream generated in oxygen gasification of organic matter. More specifically, the object of the invention is the use of the said carbon dioxide stream for carbonating the calcium used in the manufacture of paper and board. In particular, the said carbon dioxide stream comprises pure and pressurized carbon dioxide produced during the manufacture of synthetic hydrocarbon chains.

The invention is characterized in the features presented in the independent claims, and preferred embodiments of the invention are presented in the dependent claims.

Therefore, the invention relates to the use of the carbon dioxide stream generated in oxygen gasification of organic matter for carbonating calcium from a liquid containing calcium ions.

A further object of the invention is a papermaking process, in which organic matter is gasified with oxygen in order to carbonate calcium, the produced carbon dioxide stream is reacted with a liquid containing calcium ions and the carbonated calcium is added to the pulp during the papermaking process as a filler or onto finished paper as a coating.

Brief Description of the Drawings

FIG. 1 presents the oxygen gasification process of organic matter integrated into the continuous manufacturing process of calcium carbonate and papermaking.

Detailed Description of the Invention

The inventors have surprisingly found that the excess carbon dioxide produced as a by-product in biomass gasification and production of synthetic hydrocarbons may advantageously be used for carbonating calcium.

Biomass that has been treated by oxygen gasification and the carbon dioxide stream generated from this biomass for example in connection with biofuel production may be used entirely or in part, using only that part which is not used in gasification or the production process, for carbonating calcium. In the papermaking process, the carbon dioxide stream may be utilized for carbonating calcium in order to prepare a suitable amount of precipitated calcium carbonate.

Unless otherwise specified in the application, the terms used in the specification and claims have the following meanings:

The term "organic matter" refers to biomass, in other words organic matter that is of biological origin, such as wood or wood-based feed (for instance wood-based by-products of forestry and felling, for instance trees removed in thinning, stubs, rootstocks, branches, brushwood and bark), agricultural waste, municipal waste, by-products of forest industry (such as tall oil soap, tall oil, black liquor and turpentine), waste water slurry of forest industry (for instance the fibre-containing matter carried to waste water in papermaking), wasteland or plants. The raw material used may also comprise wastes or by-products of various industrial processes, marine raw materials such as algae or combinations of all the above. Preferably, the raw materials used comprise wastes or products of wood-processing industry, such as wood residue, urban wood waste, lumber waste, wood chips, sawdust, straw, firewood, wood materials, paper, by-products of papermaking and wood production, short rotation crops such as willow, poplar, black locust, eucalyptus and

lignocellulose cereal crops such as reed canary grass, Miscanthus and switchgrass. The used raw materials may also comprise vegetable oil, animal fat, fish oil, natural wax and fatty acid.

The term "synthetic hydrocarbon chain" refers to synthetically created short- and long-chain hydrocarbons.

The term "oxygen gasification" refers to gasification performed in the presence of pure oxygen (not air) and water vapour.

The present invention relates to the use of the carbon dioxide stream produced in oxygen gasification of organic matter for carbonating calcium from a liquid containing calcium ions. Preferably, the said hydrocarbon stream has been formed as a by-product of the production of synthetic hydrocarbon chains, for instance in connection with biofuel production. Preferably, at least one physical purification method that requires a high-pressure synthesis gas mixture and Fischer-Tropsch synthesis are used for producing synthetic hydrocarbon chains.

In a preferred embodiment, the said organic matter comprises biomass such as wood-based feed, agricultural waste, by-products of forest industry, waste water slurry of forest industry, or municipal waste. The wood-based feed comprises wood-based by-products of forestry and felling, for instance trees removed in thinning, stubs, rootstocks, braches, brushwood and bark.

Preferably, gasification is performed in a gasifier with a fluidized bed reactor, in which the solid biomass burns at least in part. The fluidized bed may be either a circulating or a bubbling fluidized bed, in which pure oxygen and steam are used as the fluidizing gas. Before pure oxygen and steam are led into the fluidized bed reactor, these are preferably, but not necessarily, combined with each other. Biomass is preferably fed to the gasifier by using a lockhopper. In the gasifier, solid biomass reacts endothermically with steam, forming carbon monoxide and hydrogen, and exothermically with oxygen, forming carbon monoxide, carbon dioxide and additional steam. As a result of the gasification, impure synthesis gas is thus obtained, which in addition to carbon monoxide and hydrogen

contains CO_2 (carbon dioxide), CH_4 (methane), H_2O (water), N_2 (nitrogen), H_2S (hydrogen sulphide), NH_3 (ammonia), HCl (hydrogen chloride), tar and small particles, such as ash and carbon black. The impure synthesis gas is purified and treated in several steps. For instance tar, methane and solid particles are removed therefrom. Furthermore, the hydrogen/carbon monoxide ratio of the synthesis gas is adjusted to a suitable level, after which the synthesis gas is purified by using a physical purification method such as Rectisol®, and/or a chemical purification method such as amine wash, by which for instance purified synthesis gas as well as pure and pressurized carbon dioxide are obtained. The pure synthesis gas is led for instance into a Fischer-Tropsch reactor in order to produce synthetic hydrocarbon chains.

The pure and pressurized carbon dioxide stream formed as a by-product in the production of synthetic hydrocarbon chains is especially well suited for carbonating calcium in a continuous reactor. The pure and pressurized carbon dioxide accelerates the carbonating reaction of calcium as compared to the carbon dioxide obtained from flue gases, thus enabling the use of a continuous reactor and decreasing the needed reactor size.

The regular carbon dioxide generated in a factory area and conventionally used for carbonating calcium contains a substantial amount of nitrogen. If such carbon dioxide-containing gas would be used in a pressurized state, the presence of nitrogen would lead to troublesome bubbling and foaming, since nitrogen does not dissolve in the carbonating solution. Pure pressurized carbon dioxide does not bubble or foam, since the carbon dioxide dissolves in the liquid, forming carbonic acid that reacts with calcium atoms.

The carbon dioxide obtained in the production of synthetic hydrocarbon chains is pure and high-pressurized to begin with, and it may even be led directly into a continuous carbonating reactor, where reaction times are substantially shorter than in a batch reactor. In a continuous reactor, the carbonation reaction may proceed in a matter of seconds, whereas in a batch reactor the same process may last up to several hours.

In a preferred embodiment, the purity of the carbon dioxide stream is more than 90%, preferably more than 95%, more preferably more than 97% and most preferably more than 99% by weight. The pressure of the carbon dioxide stream may be more than 5 bar,

preferably more than 20 bar, most preferably more than 30 bar. The higher the pressure, the faster the carbonation reaction. In case the pressure of the carbon dioxide stream is not sufficiently high, it may be raised by using a separate compressor to a pressure of 10 bar, preferably more than 20 bar, most preferably more than 30 bar.

The gasification according to the invention is performed by using oxygen instead of air, and in this process the nitrogen content of the synthesis gas mixture is low. This comprises one more reason why the carbon dioxide stream according to the invention is well suited especially for carbonating calcium in a continuous reactor, since a continuous process is more sensitive to impurities than a batch process. In some embodiments, the carbon dioxide stream according to the invention has a sulphur content of less than 1 ppm, and a nitrogen content of less than 10%, preferably less than 5%, more preferably less than 3%, and most preferably less than 1% by weight. Preferably, the pressure of the continuous reactor is more than 5 bar, preferably more than 10 bar, more preferably more than 20 bar, and most preferably between 20 bar and 30 bar. The low nitrogen and sulphur content of the carbon dioxide stream enables the especially advantageous carbonation of calcium in the production of precipitated calcium carbonate.

The carbon dioxide stream according to the invention may be used for carbonating calcium in a batch reactor of a batch process, or in a semi-continuous process, or in an *in-situ* papermaking process. An especially preferred combined efficiency is obtained, as the pure and pressurized carbon dioxide stream is led directly into the carbonating reaction of calcium carbonate, especially into a continuous calcium carbonate precipitation reactor.

Even though the fuels produced from biomass do not in theory add to the atmospheric carbon dioxide content since the fuels merely release the carbon dioxide bound to the biomass from air during its lifetime, also emissions created during the production process need to be taken into account. According to the invention, the carbon dioxide formed as a by-product is bound to calcium by a chemical reaction, and no carbon dioxide is therefore released into the atmosphere, making its further treatment unnecessary. As far as emission rights are concerned, the binding of carbon dioxide in the process according to the invention enables emissions in some other process. The diminished carbon dioxide amount is, of course, also commercially exploitable.

In a preferred embodiment of the invention, the gasification and/or fuel production process of organic matter is integrated into a facility for carbonating calcium, which leads to a diminished need for transports and energy savings. The gasification of organic matter and/or the production of fuel thereform, as well as the carbonation of calcium preferably take place in the same factory area, in which case the pressure of the carbon dioxide may be directly utilized in the carbonation process and the condensation and transport of carbon dioxide become unnecessary. Preferably, there is at least one papermaking process in the factory area.

An excellent combined effect is obtained, as the precipitated calcium carbonate produced in the process of the invention is used in the same factory area as a filler and/or a coating agent in the manufacture of paper and/or board.

The invention also relates to a process for producing paper or board, in which organic matter is gasified with oxygen in order to carbonate the calcium, the generated carbon dioxide stream is reacted with a liquid containing calcium ions, and the carbonated calcium is added to the pulp during the papermaking process as a filler or onto finished paper as a coating.

Preferably, the said carbon dioxide stream is formed as a by-product in the manufacture of synthetic hydrocarbons, for instance in connection with the production of biofuels, and the purity of the said carbon dioxide stream is preferably more than 90%, preferably more than 95%, more preferably more than 97%, and most preferably more than 99% by weight, and the pressure is more than 5 bar, preferably more than 10 bar, more preferably more than 20 bar, most preferably more than 30 bar. Preferably, the carbon dioxide stream according to the invention has a hydrogen sulphide content of less than 5 ppm, preferably less than 3 ppm, more preferably less than 1 ppm, and a nitrogen content of less than 10%, preferably less than 5%, more preferably less than 3% and most preferably less than 1% by weight. In a preferred embodiment, the production of the synthetic hydrocarbon chains is performed by using physical purification, such as Rectisol®, which requires high-pressurized synthesis gas mixture, preferably more than 10 bar, more preferably more than 20 bar and most preferably more than 30 bar, for which reason the synthesis gas mixture is therefore pressurized before the purification and/or Fischer-Tropsch synthesis.

In the process that is the object of the invention, the carbonation of calcium may be performed in a continuous reactor by using a pressure that is preferably more than 5 bar, preferably more than 10 bar, more preferably more than 20 bar, most preferably between 20 bar and 30 bar, in a batch process of a batch reactor or in a semi-continuous reactor. Preferably, the carbonation is integrated directly into a papermaking process. The carbonation of calcium from a calcium-containing liquid may also be performed *in-situ* in the papermaking process by adding the calcium ions and the carbon dioxide directly into the calcium-containing process liquid.

In the papermaking process, paper mass in diluted before the headbox of the paper machine by adding water, and calcium carbonate that has been carbonated according to the invention is added to the mass or, alternatively, the carbon dioxide stream according to the invention is added directly to the paper machine in order to carbonate the calcium ions.

In a preferred embodiment, the said organic matter comprises biomass, such as wood-based feed, agricultural waste, by-products of forest industry or municipal waste, wherein the wood-based feed may comprise wood-based by-products of forestry and felling, for instance trees removed in thinning, stubs, rootstocks, branches, brushwood and bark.

In one embodiment, the method comprises the manufacture of precipitated calcium carbonate, and this manufacture is adjusted according to the needs of the papermaking process, the feed of the said carbon dioxide stream being adjusted according to the calcium carbonate need. Preferably, the gasification of organic matter and/or the treatment of gas is integrated into the carbonation of the calcium and papermaking in order to efficiently utilize the formed carbon dioxide stream, thus diminishing emissions. Alternatively, the gasification of organic matter and/or treatment, the carbonation of calcium and papermaking takes place in the same factory area in order to shorten transports.

FIG. 1 presents one preferable embodiment of the invention, in which feed 1 is led into gasification 2, wherein the feed is gasified by using oxygen and steam, forming a synthesis gas mixture 3. The synthesis gas mixture 3 is objected to chemical and/or physical purification 4, by which three gas streams are obtained: a sulphur-containing gas stream 5,

a synthesis gas stream 6 and a carbon dioxide stream 7. The synthesis gas stream 6 is transferred into Fischer-Tropsch synthesis 8, by which biofuel 9 is obtained. The carbon dioxide stream 7 is led directly into paper machine 13 for the *in-situ* carbonation of calcium and/or to the continuous production of precipitated calcium carbonate in continuous reactor 10. The precipitated calcium carbonate may alternatively be prepared by a batch process. Calcium carbonate 11, 12 is led, on one hand, to a paper machine 13 to be used as a paper filler and, on the other hand, to a paper coating process 15, into which the paper moves as a paper web 14.

In a more preferred case, the wood-based by-products of the wood material purchased for manufacturing paper or board are utilized in the preparation of biofuel, and the pure and pressurized carbon dioxide obtained as a by-product is used directly in the precipitation of calcium carbonate, which is used directly in the making of paper or board.

The purpose of the following examples is only to futher illustrate the invention. By using the guidance obtained from the above description, a person skilled in the art is able to use the invention in many other ways in order to utilize the carbon dioxide stream generated in the oxygen gasification of organic matter, according to the scope of protection of the present invention.

Example 1

Gasification of biomass

Wood-based by-products formed during felling, such as trees removed in thinning, stubs, rootstocks, braches, brushwood and bark are crushed and dried. The biomass is gasified by using oxygen and steam, wherein the biomass is treated in an entrained flow gasifier at high pressure and high temperature, whereby a synthesis gas mixture comprising carbon monoxide, nitrogen and carbon dioxide is obtained as the product, and this is cooled down before purification. Thereafter the synthesis gas is purified by using the necessary chemical and physical treatments, of which the Rectisol® treatment requires that the synthesis gas mixture be pressurized to 30 bar. The purified gas is led into a Fischer-Tropsch reactor in order to form FT fuels. The conditions of the Fischer-Tropsch synthesis are selected so that the desired hydrocarbon chain length is obtained. The carbon dioxide

stream formed as a by-product in the purification of the synthesis gas mixture is used for carbonating calcium. The nitrogen content of the carbon dioxide is less than 1% by weight, and it has a pressure of 30 bar.

Example 2

Continuous preparation of precipitated calcium carbonate

A calcium hydroxide-containing water suspension and the carbon dioxide according to Example 1 (99% by weight, pressure 20 bar) are led into a reactor in an integrated production process of biofuel and calcium carbonate. The pressure of the continuous reactor is 20 bar and the calcium carbonate obtained as a product is used as a filler and a coating agent in a paper and board manufacturing process in the same factory area. For use as a filler, the carbonated calcium is added to the short circuit of a paper machine, where it is mixed with water and fibres in order to obtain the desired paper pulp. Calcium carbonate is also added onto finished paper as a coating.

Example 3

Batch production of precipitated calcium carbonate

Calcium carbonate is produced from calcium oxide by a batch process. Calcium oxide is mixed with water, whereby a calcium hydroxide-containing water suspension is obtained. The thus-obtained calcium hydroxide is carbonated with the carbon dioxide according to Example 1 (99% by weight), which is obtained from a biofuel factory located in the same factory area. Calcium carbonate and water are obtained from the reaction. The precipitated calcium carbonate is used directly as a filler and a coating agent in a papermaking process operated in the same factory area. Some of the precipitated calcium carbonate is stored and used in another manufacturing process of paper and board.

Claims

1. The use of a carbon dioxide stream generated in oxygen gasification of organic matter for carbonating calcium from a liquid containing calcium ions.

2. The use of a carbon dioxide stream according to claim 1, **characterized** in that said carbon dioxide stream is formed as a by-product of the production of synthetic hydrocarbon chains.

3. The use of a carbon dioxide stream according to claim 2, **characterized** in that said production of synthetic hydrocarbon chains comprises production of biofuels.

4. The use of a carbon dioxide stream according to claim 2 or 3, **characterized** in that the production of synthetic hydrocarbon chains comprises physical purification that requires pressurized synthesis gas mixture and/or the use of a Fischer-Tropsch synthesis.

5. The use of a carbon dioxide stream according to any one of the above claims, **characterized** in that said organic matter comprises biomass, for instance wood-based feed, agricultural waste, by-products of forest industry, waste water slurry of forest industry or municipal waste.

6. The use of a carbon dioxide stream according to claim 5, **characterized** in that said wood-based feed comprises wood-based by-products of forestry and felling, for instance trees removed in thinning, stubs, rootstocks, braches, brushwood and bark.

7. The use of a carbon dioxide stream according to any one of the above claims, **characterized** in that the purity of the carbon dioxide stream is more than 90%, preferably more than 95%, more preferably more than 97%, and most preferably more than 99% by weight.

8. The use of a carbon dioxide stream according to any one of the above claims, **characterized** in that the pressure of the carbon dioxide stream is more than 5 bar,

preferably more than 10 bar, more preferably more than 20 bar, most preferably more than 30 bar.

9. The use of a carbon dioxide stream according to any one of the above claims, **characterized** in that the sulphur content of the carbon dioxide stream is less than 1 ppm.

10. The use of a carbon dioxide stream according to any one of the above claims, **characterized** in that said carbon dioxide stream contains less than 10%, preferably less than 5%, more preferably less than 3%, most preferably less than 1% by weight of nitrogen.

11. The use of a carbon dioxide stream according to any one of the above claims, **characterized** in that the calcium is carbonated in a continuous reactor.

12. The use of a carbon dioxide stream according to claim 11, **characterized** in that the pressure of the continuous reactor is more than 5 bar, preferably more than 10 bar, more preferably more than 20 bar, most preferably between 20 and 30 bar.

13. The use of a carbon dioxide stream according to any one of claims 1 to 10, **characterized** in that the calcium is carbonated in a batch reactor or in a semi-continuous reactor.

14. The use of a carbon dioxide stream according to any one of claims 1 to 10, **characterized** in that the calcium is carbonated *in-situ* in a papermaking process.

15. The use of a carbon dioxide stream according to any one of the above claims, **characterized** in that the gasification of organic matter is integrated into the carbonation of calcium in order to enable the utilization of the generated carbon dioxide stream.

16. The use of a carbon dioxide stream according to any one of claims 1 to 14, **characterized** in that the gasification of organic matter and the carbonation of calcium take place in the same factory area in order to enable the utilization of pressure of the carbon dioxide.

17. A process for preparing paper or board, **characterized** in that organic matter is gasified with oxygen in order to carbonate the calcium, the generated carbon dioxide stream is reacted with a liquid containing calcium ions, and the carbonated calcium is added to the pulp as a filler and/or onto finished paper as a coating during the manufacture of paper or board.

18. A process according to claim 17, **characterized** in that said carbon dioxide stream is generated as a by-product in the production of synthetic hydrocarbon chains.

19. A process according to claim 18, **characterized** in that said production of synthetic hydrocarbon chains comprises the production of biofuels.

20. A process according to claim 18 or 19, **characterized** in that the synthesis gas mixture obtained by said oxygen gasification is purified by physical purification that requires pressurization of the synthesis gas mixture and/or that said synthetic hydrocarbon chains are formed by Fischer-Tropsch synthesis.

21. A process according to any one of claims 17 to 20, **characterized** in that said organic matter is biomass such as wood-based feed, agricultural waste, by-products of forest industry, waste water slurry of forest industry or municipal waste.

22. A process according to claim 21, **characterized** in that said wood-based feed comprises wood-based by-products of forestry and felling, such as trees removed in thinning, stubs, rootstocks, braches, brushwood and bark.

23. A process according to any one of claims 17 to 22, **characterized** in that the purity of said carbon dioxide stream is more than 90%, preferably more than 95%, more preferably more than 97%, and most preferably more than 99% by weight.

24. A process according to any one of claims 17 to 23, **characterized** in that the pressure of said carbon dioxide stream is more than 5 bar, preferably more than 10 bar, more preferably more than 20 bar, most preferably more than 30 bar.

25. A process according to any one of claims 17 to 24, **characterized** in that said carbon dioxide stream contains less than 1 ppm of sulphur.

26. A process according to any one of claims 17 to 25, **characterized** in that said carbon dioxide stream contains less than 10%, preferably less than 5%, more preferably less than 3%, and most preferably less than 1% by weight of nitrogen.

27. A process according to any one of claims 17 to 26, **characterized** in that the carbonation of calcium is adjusted according to the needs of the papermaking process and the use of said carbon dioxide stream is adjusted according to the calcium carbonate need.

28. A process according to any one of claims 17 to 27, **characterized** in that calcium is carbonated in a continuous reactor.

29. A process according to claim 28, **characterized** in that the pressure of said continuous reactor is more than 5 bar, preferably more than 10 bar, more preferably more than 20 bar, most preferably between 20 and 30 bar.

30. A process according to claim 28 or 29, **characterized** in that said continuous reactor is integrated into a papermaking process.

31. A process according to any one of claims 17 to 27, **characterized** in that calcium is carbonated in a batch reactor or in a semi-continuous reactor.

32. A process according to any one of claims 17 to 27, **characterized** in that calcium is carbonated *in-situ* in a papermaking process.

33. A process according to any one of claims 17 to 32, **characterized** in that the gasification of organic matter is integrated into the carbonation of calcium and the manufacture of paper or board in order to enable the utilization of the generated carbon dioxide stream.

34. A process according to any one of claims 17 to 32, **characterized** in that the gasification of organic matter, the carbonation of calcium and the manufacture of paper or board take place in the same factory area.

Fig. 1

