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(54) PROCESS FOR PRODUCING SODIUM CARBONATE

(57) A method for the manufacture of sodium carbonate or sodium bicarbonate, wherein said method comprises a limestone calcining step in a vertical shaft lime-kiln, to produce lime (CaO) and a gas comprising carbon dioxide (CO_2), using a limestone and a carbonaceous combustible,
wherein said carbonaceous combustible comprises at least partly a biochar, compacted into briquettes, using one or several inorganic or organic binding agents, and wherein said briquettes having a particle size distribution so that:
- at most 20% in weight of the briquettes are of size of more than 90 mm,
- and at most 20% in weight of the briquettes are of size of less than 25 mm characterized in that:
- the mass amount of the biochar reported to the briquette mass is at least 15 wt. % dry;
- the briquettes comprise preferably at most 50 wt.% volatile matter;
- the amount of the binding agent(s) and the compacting pressure are adjusted so that less than 2% by weight of briquette fines under 5 mm are generated by a fall of 6 meters-high of briquettes, dropped individually and quantified as a mean value measured on a sample of at least 5 briquettes from said carbonaceous combustible.

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Description

Technical field

[0001] The invention relates to an improved process for producing sodium carbonate or sodium bicarbonate, wherein said method comprises a limestone calcining step in a limekiln, to produce lime (CaO) and a limekiln gas comprising carbon dioxide (CO_2), using a limestone and a carbonaceous combustible.

[0002] The invention pertains more particularly to a production process featuring reduced emission of carbon dioxide (CO_2) from fossil fuel(s) such as natural gas, oil or coal, for producing sodium carbonate, or of a process for producing refined bicarbonate. The invention relates also to a carbonaceous combustible coated with a delaying combustion compound, which enables to improve the use of biochar, such as biochar lumps or biochar briquettes in limekilns for sodium carbonate or sodium bicarbonate manufacturing.

[0003] In the present specification, a process for producing sodium carbonate with ammonia, also referred to as the Solvay process, means a process utilizing sodium chloride (NaCl), ammonia (NH_3) and carbon dioxide (CO_2) for the production of sodium bicarbonate (ammoniacal crude sodium bicarbonate) according to the following reactions:

$$NaCl + H_2O + NH_3 \leftrightarrow NaCl + NH_4OH \qquad (1)$$

$$NaCl + NH_4OH + CO_2 \leftrightarrow NaHCO_3(solid) + H_2O + NH_4Cl \qquad (2)$$

[0004] The sodium bicarbonate (ammoniacal crude sodium bicarbonate) may be subsequently calcined to give sodium carbonate (light soda ash) according to the following reaction:

$$2\ NaHCO_3(solid) \rightarrow Na_2CO_3(solid) + H_2O(gas) + CO_2(gas) \qquad (3)$$

[0005] In a first variant of the Solvay process, the ammonium chloride (NH_4Cl) is regenerated to gaseous ammonia by reaction with an alkali, generally lime or caustic soda, followed by distillation. For example, with hydrated lime ($Ca(OH)_2$), according to the following reaction:

$$2\ NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2\ NH_3 + 2\ H_2O \qquad (5)$$

and the ammonia (gaseous) is recovered, generally by distillation.

[0006] The lime is generally produced by calcining limestone with coke, to produce quicklime, according to the following reaction:

$$CaCO_3 \rightarrow CaO + CO_2(gas) \qquad (6)$$

and the quicklime is then hydrated in the form of milk of lime to produce calcium hydroxide ($Ca(OH)_2$).

[0007] In a second variant of the process, when the preference is for utilizing the ammonium chloride in the form of a finished product, the ammonium chloride is crystallized in a fourth step (4) by addition of solid sodium chloride and by cooling; in this way, ammonium chloride is precipitated, and can be used, for example, as a fertilizer. This second variant is accompanied by a net consumption of ammonia, according to the molar amount of ammonia extracted from the process which is not regenerated and not recycled. This variant of the Solvay process with ammonia is generally referred to as the dual process or Hou process.

[0008] The present invention may be applied to either of the two variants, the basic reactions in which are described above.

[0009] In one or the other variant, the production of "refined sodium bicarbonate" (" refined" in contrast to the ammoniacal crude bicarbonate) is carried out in general from solid sodium carbonate dissolved in aqueous solution, and the solid sodium bicarbonate is recrystallized and purified according to the following reaction:

$$Na_2CO_3(solution) + H_2O(gas) + CO_2(gas) \rightarrow 2\ NaHCO_3(solid) \qquad (7)$$

[0010] Sodium carbonate or refined sodium bicarbonate may also be produced from sodium carbonate obtained by other processes, such as a sodium carbonate monohydrate process or a sodium sesquicarbonate process, using trona or nahcolite minerals as raw material. Said processes may also be in need of lime (CaO) or milk of lime ($Ca(OH)_2$) to chemically calcine part of the bicarbonate ions in aqueous solution in said processes using natural minerals.

[0011] Sodium carbonate is an essential chemical used in particular for the production of flat glass (used for instance for windows of building and houses, wherein its use has a net positive CO_2 balance, with the heat energy it enables to provide with natural sun heating, in particular in double shield insulated windows either in cold or hot regions. Flat glass is also used to protect photovoltaic panels from rain, ice or snow. And as such, the sodium carbonate needs are still increasing at about 2% in volume per year.

[0012] Sodium bicarbonate has plenty of uses such as the food and feed industry, in the pharmaceutical industry and services (effervescent tabs, digestive formulations, blood hemodialysis for children and adults), and in the gas treatment industry to mitigate acidic gasses such as HCl, SOx, and others.

[0013] Fossil CO_2 decarbonation of existing chemical processes is a global concern to curb down, in the 20 years to come, the global anthropogenic CO_2 and other greenhouse gases emissions, so that to stabilize and then rapidly reduce the greenhouse gasses in the Earth atmosphere generated by human beings.

[0014] Present sodium carbonate production units use fossil energy (natural gas, oil, or coal) mainly on two main sectors: steam generators and in lime kilns to produce the quicklime and the CO_2 necessary for producing sodium carbonate and sodium bicarbonate:

- the steam generator sector may use alternative non-fossil energy such as nuclear energy (either in electricity form or in heat form), or decarbonized electricity (such as the one from hydraulic origins, or from photovoltaic, or from wind power, or from sea streams power), or biomass;
- the lime kiln sector producing lime (CaO) and carbon dioxide (CO_2) out of limestone ($CaCO_3$), need energy to calcine limestone ($CaCO_3$) into lime (CaO) and CO_2 at high temperature typically from 900° to 1250°C. Even if certain equipment manufacturers have proposed limekilns using electricity, the electrical resistances at 900 to 1250°C have demonstrated, in quarry type environment, poor mechanical resistance and short live duration of such equipment parts. Therefore, no acceptable technical solution exists presently for using decarbonized electricity in this usage of limestone calcination for equipment of large size needed in plants producing one or several hundred thousand tons per year of lime.

Prior art

[0015] The Solvay process for producing sodium carbonate (also called soda ash) has undergone numerous developments and optimizations over 150 years, since its creation by Ernest Solvay. These developments have included in particular its energy optimization and the improved management of CO_2.

[0016] An example of the process for producing sodium carbonate according to the ammonia process, and of the production of refined bicarbonate, is described in Ullmann's Encyclopedia of Industrial Chemistry ("Sodium carbonate" chapter, 2002 edition, Wiley-VCH Verlag GmbH & Co., 24 pages, in paragraphs 1.4.1 and 1.4.2).

[0017] Limekilns in sodium carbonate plants generally use coke or coal as source of energy.

[0018] Theoretically, in the soda ash process, the CO_2 balance is stoichiometrically neutral. However, a CO_2 excess is needed to compensate the incomplete absorption of CO_2 in the carbonation stage, and minor losses in the treatment of the mother liquid in the distillation area. This CO_2 excess is generated by combustion of solid carbonized fuel as mentioned supra. Said solid carbonized fuels provide the energy used for limestone decomposition and is an additional source of CO_2.

[0019] The operating conditions of a limekiln fitted to soda ash production are different from those used for lime production in civil engineering or for metallurgy. This, because for soda ash production there is a need to produce a gas with the maximum concentration of carbon dioxide for its subsequent use in the process. This is done generally to the detriment of the purity of the produced lime, which will contain unburnt limestone to favor high CO_2 content in the kiln gas. Said unburnt limestone is generally recycled back in the limekiln after screening the unburnt solid, present in the coarser size fraction when sieving the produced milk of lime. To improve the particle size of limestone loaded into the limekiln, screening is carried out prior to kiln loading.

[0020] Presently, there is no use of biochar in limekilns for producing sodium carbonate or sodium bicarbonate.

[0021] Fresh biomass or wood have generally a volatile content of 75 to 80 weight % on dry matter. When dried biomass or wood is used in limekilns for the production of sodium carbonate or bicarbonate, the CO_2 content of the limekiln gas (e.g. reaction (6) supra) falls far lower than 40% in volume, on dried gas. It generally reaches 35 down to 20 vol. % of CO_2 expressed on dry gas which increases the cost of compression of said lime kilns in CO_2 absorbers, and drops sensitively the yield of CO_2 absorption in CO_2 absorbers and other equipment (e.g. reactions (2), (3), and (7) supra). This generates a release of CO_2 in the atmosphere with residual gasses, and a net loss of carbon in the process.

[0022] Presently, only fossil carbonaceous combustible are used in limekilns for producing sodium carbonate or bicarbonate and not biochar or charcoal. The most used combustible in said productions, is metallurgical coke, or hard coal when coke is insufficiently available. Present requirements of said used fossil carbonaceous combustible are less than 4% or less than 3% of volatile matter.

[0023] Higher volatiles content induces high concentration of methane (CH_4), dihydrogen (H_2) and carbon monoxide (CO) in the limekiln gas when operating them for sodium carbonate or bicarbonate manufacturing. This is the case in particular when changing the operating rate of said limekilns, as during unsteady operating conditions said inflammable gasses concentration may be multiplied by a factor 2 or 3 in the produced limekiln gas.

[0024] Such inflammable and explosive gasses have generated several severe accidents in the past. Therefore, sodium carbonate and bicarbonate manufacturers refuse to use carbonaceous combustibles having volatile higher than 3% or 4%. Typical values of volatile matter in fossil carbonaceous combustible used in limekilns for sodium carbonate and bicarbonate manufacturing is 0 to 3% (0 - 30 kg/ t combustible): see European Union - IPPC BAT Reference Document - Process BREF for Soda Ash manufacturing - March 2004 - ESAPA - Issue 3 - Table 6 page 30.

[0025] Therefore, in order to decarbonize soda ash processes from fossil carbon in limekilns, biochar could not been envisioned as biochar or charcoal have a high volatile matter. Indeed biochar and charcoal produced by carbonizing: biomass, natural wood, waste wood, pruning, branches, by-products of fruit stones (such as olive stone, peach stone, walnut shell, hazelnut shell, almond shell, etc.), wood furniture wastes, drinking or waste water treatment plant muds, have generally a volatile content much higher than fossil fuel used in limekilns for producing sodium carbonate or bicarbonate.

[0026] Raw biomass has generally a volatile matter of about 75 to 80 wt. %. And biochar produced from it has a volatile matter in general higher than 3.5 wt.% on dry mass, typically from 3.5 to 25 wt.%; and can reach up 35 wt.% or 50 wt. % of volatile matter with torrefied wood or biomass.

[0027] Moreover biochar has a combustion with air generating in the combustion gas generally more soot and secondary decomposition products, such as sulfur compounds, nitrogen compounds, phosphor compounds, pyrolitic organics, acidic organic compounds, terpens and the likes. Those secondary decomposition products are generally of dark or black colors and are detrimental when such combustion gases are used to synthetize white products such as sodium carbonate crystals or sodium bicarbonate crystals. Also, the said pyrolitic decomposition products and related organics compounds, have a tendency to polymerize and condensate with vapor on cold surfaces or when cooled down, forming bio-oil which is also of dark-brown or black color, and that are detrimental for the quality of the final products when the said combustion gases are used as CO_2 source in the synthesis of sodium carbonate or bicarbonate.

Brief description of the invention

[0028] The inventors of present invention have surprisingly observed that when using biochar, the operating conditions as listed in item 1 infra, and in the related items, enable to limit sensitively the generation of inflammable gas such as CH_4, H_2, and CO, enable to produce a limekiln gas comprising at least 35% vol. CO_2 or higher concentration, reduces the generation of PAHs (Polycyclic Aromatic Hydrocarbons) and BTEX (such as Benzene, Toluene, Ethylbenzene, and Xylene isomers) by a factor 2 to 6, compared to fossil fuels in the produced limekiln gas.

[0029] As with volatile matter above 35 wt%, and particularly above 50 wt% when biocarbon is used:

- the obtained limekiln gas has a significant decrease of the CO_2 content on the generated limekiln gas: below 37 or even below 35 vol. % on dry gas;
- the percentage of inflammable gas such as methane (CH_4), dihydrogen (H_2), carbon monoxide (CO), released by the biochar combustible in neutral atmosphere (ie nitrogen N_2 sweeping gas) when heating it up to 900°C, reported by weight of biochar, increase significantly with values above 2 wt. % equivalent of H_2 in said atmosphere so close to hydrogen lower explosion limit of 3.5 wt% H_2 (4 vol. % H_2 equivalent) in presence of a gas with 2 vol. % of oxygen concentration which is representative of typical composition in oxygen in produced limekiln gas for sodium carbonate manufacturing. Indeed this increases security risks when said limekiln gas is handled thereafter in mechanical compressors before their use in the manufacturing of sodium carbonate and/or bicarbonate.

[0030] Moreover, the inventors have observed that Tars, PAHs (Polycyclic Aromatic Hydrocarbons) and BTEX (compounds such as Benzene, Toluene, Ethylbenzene, and Xylene isomers) compounds increase sensitively in the limekiln gas when the volatile content of the biochar is above 50 wt% on dry base. The same regarding phenolic compounds. Said components are toxic and do not fit the requirements for producing food or pharmaceutical products, and induce costly gas treatment on residual gasses before released in the environment. They are detrimental to the operation of limekilns as part of them condense on colder parts of the gas circuits accumulating toxic compounds. Therefore, the biochar or charcoal should comprise at most 50 wt % preferably at most 35 wt. % of volatile matter in weight for their use in sodium carbonate or bicarbonate manufacturing.

[0031] Additionnally the inventors of present invention have surprisingly observed that when using briquettes comprising biochar, the fines of briquettes generated during briquette transport, handling, and limekiln loading release and desorb said inflammable gasses, such as H2, CH4 and CO associated with biochar pyrolysis, much more faster than the coarse fraction of briquettes.

[0032] This increases the risk of accident associated with inflammable matter in limekiln gas close to the explosive limit of said gas, in particular when the air ventilator of the limekiln sees a decrease of its flow, and/ or when it is stopped due to incidents.

[0033] Therefore, operating conditions as listed in items 1 and 4 infra with related other items, limit sensitively the negative impacts listed supra generated by the fine particles of fragile briquettes during the limekiln operations, and improve the yield of the carbonaceous use of the biochar content of the briquettes, while mitigating the effect of high volatile matter in briquettes comprising biochar. Therefore the present invention relates to a method for the manufacture of sodium carbonate or sodium bicarbonate,

wherein said method comprises a limestone calcining step in a vertical limekiln, to produce lime (CaO) and a limekiln gas comprising carbon dioxide (CO_2), using a limestone and a carbonaceous combustible,
wherein said carbonaceous combustible comprises at least partly a biochar, compacted into briquettes using one or several binding agents selected among:

- one or several inorganic binder(s) and/ or
- one or several organic binder(s), and

the binding agent(s) being used in an amount expressed as the dry amount of the binding agent reported to total weight of the dry briquettes,
wherein the binding agent(s) is(are) mixed with the carbonaceous combustible to form a mixture, the mixture is compacted at a compacting pressure in a matrix or in a screw into briquettes, the obtained briquettes are then optionally thermally cured,
said briquettes having a particle size distribution so that:

- at most 20% in weight of the briquettes are of size of more than 90 mm,
- and at most 20% in weight of the briquettes are of size of less than 25 mm characterized in that:
  - the mass amount of the biochar reported to the briquette mass is at least 15 wt. % dry;
  - the amount of the binding agent(s) and the compacting pressure are adjusted so that less than 2% by weight of briquette fines under 5 mm are generated by a fall of 6 meters-high of briquettes, dropped individually and quantified as a mean value measured on a sample of at least 5 briquettes from said carbonaceous combustible.

[0034] The invention relates also to a method for the manufacture of sodium carbonate or sodium bicarbonate,

wherein said method comprises a limestone calcining step in a vertical shaft limekiln, to produce lime (CaO) and a gas comprising carbon dioxide (CO_2), using a limestone and a carbonaceous combustible,
wherein said carbonaceous combustible comprises at least partly a biochar, compacted into briquettes using one or several binding agents selected among:

- one or several inorganic binder(s) and/ or
- one or several organic binder(s), and

the binding agent(s) being used in an amount expressed as the dry amount of the binding agent reported to total weight of the dry briquettes,
wherein the binding agent(s) is(are) mixed with the carbonaceous combustible to form a mixture, the mixture is compacted at a compacting pressure in a matrix or in a screw into briquettes, the obtained briquettes are then optionally thermally cured,
said briquettes having a particle size distribution so that:

- at most 20% in weight of the briquettes are of size of more than 90 mm,
- and at most 20% in weight of the briquettes are of size of less than 25 mm characterized in that:
  - the mass amount of the biochar reported to the briquette mass is at least 30 wt. % dry;
  - the briquettes comprise at most 50 wt.% volatile matter;
  - the amount of the binding agent(s) and the compacting pressure are adjusted so that the cold mechanical strength according to ISO 556:2020 (half drum) on briquettes of size of at least 20 mm, has a Micum Index M10 (< 10mm) of at most 25 wt.%.

[0035] The present invention relates also on a carbonaceous combustible such as: charcoal, charcoal briquette, coke briquette, or anthracite briquette, coated with a layer comprising a compound selected among: cement, starch, limestone, and mixtures thereof, and wherein the weight of the layer after drying at 50°C and reported to the carbonaceous combustible weight is at least 4% and at most 35%.

[0036] Indeed the inventors of the present invention have observed that the hot strength temperature of the said carbonaceous combustible can be increased from 50° to 100°C with such coatings.

[0037] This is important as the hot strength of carbonaceous combustible is an important feature when used in a soda ash limekiln. Indeed when the carbonaceous combustible has a low hot strength, the combustible fragments itself in several pieces when submitted to a mechanical constraint and such fragmented pieces of the combustible burn in a faster way than coarser pieces of combustible. This has the consequence to enlarge the fire zone in limekilns, such as: vertical shaft kilns, or rotary kilns.

Definitions

[0038] In the present descriptive specification, some terms are intended to have the following meanings.

[0039] The term 'biochar' is intended to mean a carbonized (in general from a thermochemical reaction in an oxygen-limited environment) carbonaceous combustible or a charcoal, originated from biomass, such as a vegetal or from a marine origin. Example of such feedstock to be carbonized can be:

natural wood, waste wood, pruning, branches, by-products of fruit stones (such as olive stone, peach stone, walnut shell, hazelnut shell, almond shell, etc.),

wood furniture wastes, wood waste in particular wood waste of class B (according to UNECE-FAO United Nations wood waste classification catalogue 2022), drinking water or waste water treatment plant muds, paper industry mud, lignocellulosic wastes, algae, phytoplankton, etc.....

[0040] The term 'carbonaceous combustible' is intended to mean a combustible comprising carbon, which generates carbon dioxide (CO_2) when it is burnt with air or with oxygen.

[0041] In the present specification, the volatile matter content is measured according to ISO 562:2010 standard.

[0042] In the present specification, the fixed carbon content is measured according to ISO 17246 standard.

[0043] In the present specification, the moisture content is measured according to ISO 11722:2013 standard.

[0044] In the present specification, the ash content is measured according to ISO 1171:2010 standard.

[0045] In the present specification, the composition of the volatile matter in CH_4, H_2, and CO, is measured according to the operating mode described in example 1 by pyrolyze with nitrogen gas sweeping, following a heating profile of 20°C/minutes up to 900°C and then a plateau at 900°C during 7 minutes (similar to ISO 562:2010 standard for total volatile matter determination).

[0046] In the present specification, the choice of an element from a group of elements also explicitly describes:

- the choice of two or the choice of several elements from the group,
- the choice of an element from a subgroup of elements consisting of the group of elements from which one or more elements have been removed.

[0047] In the present specification, the description of a range of values for a variable, defined by a bottom limit, or a top limit, or by a bottom limit and a top limit, also comprises the embodiments in which the variable is chosen, respectively, within the value range: excluding the bottom limit, or excluding the top limit, or excluding the bottom limit and the top limit.

[0048] The term "comprising" includes "consisting essentially of" and also "consisting of".

[0049] The use of "one" or "a(n)" in the singular also comprises the plural, and vice versa, unless otherwise indicated.

[0050] In the present specification, the terms "%", "% by weight", "wt%", "wt. %", "weight percentage", or "percentage by weight" can be used interchangeably, unless the "%" term is explicitly referred to an other physical unit (such as for instance "% in volume" or "vol. %", etc....

[0051] If the term "about" is used before a quantitative value, this corresponds to a variation of ± 10% of the nominal quantitative value, unless otherwise indicated.

Detailed description of the invention

[0052] A first advantage of the present invention is to reduce the footprint of fossil carbon dioxide (CO_2) when manufacturing sodium carbonate or sodium bicarbonate by using a carbonaceous combustible comprising at least partly biochar.

[0053] A second advantage of the present invention is to improve the security of limekilns operation and operators when using briquettes comprising biochar, by avoiding to reach explosive concentrations of gasses such as: carbon monoxide (CO), methane (CH_4), and dihydrogen (H_2).

[0054] A third advantage of the present invention is to improve the limekiln operation with a limited spread of the fire zone in the limekiln when using briquettes comprising biochar.

[0055] A fourth advantage of the present invention is to enable the generation of a limekiln gas with lower PAHs (Polycyclic Aromatic Hydrocarbons), BTEX (Benzene, Toluene, Ethylbenzene, and Xylene isomers) than the limekiln gas obtained with fossil carbonaceous fuels such as hard coal, anthracite, or metallurgical coke briquettes.

[0056] A fifth advantage of the present invention is to enable the generation of a limekiln gas with limited soot, and secondary decomposition products, such as: pyrolitic organics, terpens, furans, aldehydes, and carboxylic acids when using briquettes comprising biochar.

[0057] A sixth advantage of the present invention is to limit the generation colored dust and of colored compounds and molecules in the limekiln gas, avoiding the coloration of sodium carbonate or bicarbonate.

[0058] A seventh advantage of the present invention, linked to the fourth to sixth advantages above, is to generate a gas compatible with the manufacture of sodium carbonate or bicarbonate of food grade and/or of pharmaceutical grade.

[0059] A eighth advantage of the present invention is to enable the generation of a high CO_2 content in the generated limekiln gas, used in the sodium carbonate or sodium bicarbonate manufacturing process.

[0060] A ninth advantage of the present invention is to enable a smooth operation of limekilns and CO_2 compressor sector when using briquettes comprising biochar avoiding the polymerization and condensation of organics on cold surfaces that plug equipment and rotary compressors.

[0061] A tenth advantage of the present invention, when using briquettes comprising biochar rather than fossil fuel such as coke and anthracite, is to reduce the concentration of SO_2 in the limekiln gas and of gypsum in the milk of lime. The latter plug the distiller sector equipment and related pipes reducing their operation time between cleaning operation steps when producing sodium carbonate or bicarbonate.

[0062] An eleventh advantage of the present invention when using briquettes comprising partly or totally biochar in replacement of fossil carbonaceous combustible fed in limekilns is to reduce the insolubles comprising oxides of silicon, aluminum and/or iron in liquid effluents from ammonia distillation sector when manufacturing sodium carbonate. This leads also to a decrease of solid incrustation on surfaces of distillation equipment when producing sodium carbonate and using said biochar in replacement of fossil carbonaceous combustibles.

[0063] The present invention relates to a number of embodiments of the process, which are detailed below.

[0064] Item 1. A method for the manufacture of sodium carbonate or sodium bicarbonate,

> wherein said method comprises a limestone calcining step in a vertical limekiln, to produce lime (CaO) and a limekiln gas comprising carbon dioxide (CO_2), using a limestone and a carbonaceous combustible,
> wherein said carbonaceous combustible comprises at least partly a biochar, compacted into briquettes using one or several binding agents selected among:
>
> - one or several inorganic binder(s) and/ or
> - one or several organic binder(s), and
>
> the binding agent(s) being used in an amount expressed as the dry amount of the binding agent reported to total weight of the dry briquettes,
> wherein the binding agent(s) is(are) mixed with the carbonaceous combustible to form a mixture, the mixture is compacted at a compacting pressure in a matrix or in a screw into briquettes, the obtained briquettes are then optionally thermally cured,
> said briquettes having a particle size distribution so that:
>
> - at most 20% in weight of the briquettes are of size of more than 90 mm,
> - and at most 20% in weight of the briquettes are of size of less than 25 mm characterized in that:
>   - the mass amount of the biochar reported to the briquette mass is at least 15 wt. % dry;
>   - the amount of the binding agent(s) and the compacting pressure are adjusted so that less than 2% by weight of briquette fines under 5 mm are generated by a fall of 6 meters-high of briquettes, dropped individually and quantified as a mean value measured on a sample of at least 5 briquettes from said carbonaceous combustible.

[0065] Item 2. The method of the preceding item wherein the amount of the binding agent(s) and the compacting pressure are adjusted so that less than 1.5% by weight of briquette fines under 5 mm are generated by a fall of 6 meters-high of briquettes, dropped individually and quantified as a mean value measured on a sample of at least 5 briquettes from said carbonaceous combustible.

[0066] Item 3. The method of the preceding item wherein the amount of the binding agent(s) and the compacting pressure are adjusted so that less than 1.0% by weight of briquette fines under 5 mm are generated by a fall of 6 meters-high of briquettes, dropped individually and quantified as a mean value measured on a sample of at least 5 briquettes from said carbonaceous combustible.

[0067] Item 4. A method for the manufacture of sodium carbonate or sodium bicarbonate according to the Solvay ammonia process,

wherein said method comprises a limestone calcining step in a vertical shaft limekiln, to produce lime (CaO) and a gas comprising carbon dioxide (CO_2), using a limestone and a carbonaceous combustible,
wherein said carbonaceous combustible comprises at least partly a biochar, compacted into briquettes using one or several binding agents selected among:

- one or several inorganic binder(s) and/ or
- one or several organic binder(s), and

the binding agent(s) being used in an amount expressed as the dry amount of the binding agent reported to total weight of the dry briquettes,
wherein the binding agent(s) is(are) mixed with the carbonaceous combustible to form a mixture, the mixture is compacted at a compacting pressure in a matrix or in a screw into briquettes, the obtained briquettes are then optionally thermally cured,
said briquettes having a particle size distribution so that:

- at most 20% in weight of the briquettes are of size of more than 90 mm,
- and at most 20% in weight of the briquettes are of size of less than 25 mm characterized in that:
    - the mass amount of the biochar reported to the briquette mass is at least 30 wt. % dry;
    - the biochar comprises at most 50 wt.% volatile matter;
    - the amount of the binding agent(s) and the compacting pressure are adjusted so that the cold mechanical strength according to ISO 556:2020 (half drum) on briquettes of size of at least 20 mm, has a Micum Index M10 (< 10mm) of at most 25 wt.%.

[0068] Item 5. The method of any preceding items wherein the biochar comprises at most 35 wt. % or at most 30 wt. % volatile matter.

[0069] Item 6. The method of any of the preceding items wherein the biochar comprises at most 17 wt. % or at most 15 wt. % volatile matter.

[0070] Item 7. The method of any of the preceding items wherein the biochar comprises at least 3%, preferably at least 3.5% by weight of volatile matter on a dry base.

[0071] Item 8. The method of any of the preceding items wherein the biochar comprises at least 5%, preferably at least 6% by weight of volatile matter on a dry base.

[0072] Item 9. The method of any of the preceding items wherein the biochar comprises at least 6% and at most 16% by weight of volatile matter on a dry base.

[0073] Item 10. The method of any of the preceding items wherein the biochar comprises at least 16% and at most 27% by weight of volatile matter on a dry base.

[0074] Item 11. The method of any of the preceding items wherein the biochar comprises at most 2 wt. % or at most 1.5 wt. % as H_2 in volatile matter reported to total weight of dried biochar.

[0075] Item 12. The method of any of the preceding items wherein the briquettes comprise at most 2 wt. % or at most 1.5 wt. % as H_2 in volatile matter reported to total weight of dried briquettes.

[0076] Item 13. The method of any of the preceding items wherein the briquettes comprise at most 50 wt. % or at most 35 wt. % volatile matter.

[0077] Item 14. The method of any of the preceding items wherein the briquettes comprise at most 30 wt. % or at most 20 wt. % volatile matter.Item 15. The method of any of the preceding items wherein the briquettes comprise at most 15 wt. % or at most 12 wt. % volatile matter.

[0078] Item 16. The method of the preceding item, wherein the briquettes comprise at most 10 wt.% or at most 7 wt. % volatile matter.

[0079] Item 17. The method of the preceding item, wherein the briquettes comprise at most 4 wt% volatiles matter.

[0080] Item 18. The method of any of the preceding items wherein the briquettes comprise at least 6% and at most 17% by weight of volatile matter on a dry base.

[0081] Item 19. The method of any of the preceding items wherein the briquettes comprise at least 17% and at most 27% by weight of volatile matter on a dry base.

[0082] Item 20. The method of any of the preceding items, wherein the briquettes comprise at most 85 wt%, preferably at most 75 wt. % of coke or of anthracite on a dry base.

[0083] Item 21. The method of any of the preceding items, wherein the briquettes comprise at most 65 wt%, preferably at most 55 wt. % of coke or of anthracite on a dry base.

[0084] Item 22. The method of any of the preceding items, wherein the briquettes comprise at most 45 wt%, preferably at most 35 wt. % of coke or of anthracite on a dry base.

[0085] Item 23. The method of the preceding item, wherein the briquettes comprise at most 25 wt%, preferably at most 15 wt% of coke or of anthracite on a dry base.

[0086] Item 24. The method of any one of the preceding items, wherein the briquettes comprise at least 20 wt% or at least 25 wt.% of biochar on a dry base.

[0087] Item 25. The method of the preceding item, wherein the briquettes comprise at least 30 wt% or at least 35 wt% of biochar on a dry base.

[0088] Item 26. The method of the preceding item, wherein the briquettes comprise at least 40 wt% or at least 50 wt% of biochar on a dry base.

[0089] Item 27. The method of the preceding item, wherein the briquettes comprise at least 60 wt% at least 70 wt% of biochar on a dry base.

[0090] Item 28. The method of the preceding item, wherein the briquettes comprise at least 75 wt% or at least 85 wt% of biochar on a dry base.

[0091] Item 29 The method of the preceding item, wherein the briquettes comprise at least 90 wt% or at least 95 wt% of biochar on a dry base.

[0092] Item 30. The method of any one of the preceding items, wherein the briquettes are devoid of fossil fuel such as coke, pet coke, anthracite, lignite, or coal.

[0093] Item 31. The method of any one of the preceding items, wherein the briquettes comprise at most 25 wt%, or at most 20 wt% of the binding agent on a dry base.

[0094] Item 32. The method of the preceding item, wherein the briquettes comprise at most 15 wt%, or at most 12 wt% of the binding agent on a dry base.

[0095] Item 33. The method of the preceding item, wherein the briquettes comprise at most 10 wt%, or at most 8 wt% of the binding agent on a dry base.

[0096] Item 34. The method of the preceding item, wherein the briquettes comprise at most 8 wt%, or at most 6 wt% of the binding agent on a dry base.

[0097] Item 35. The method of any one of the preceding items, wherein the sum of the weight of biochar, plus the weight of coke or anthracite, plus the weight of the binding agent is 100 wt% of the briquettes on a dry base.

[0098] Item 36. The method of any one of the preceding items, wherein the sum of the weight of biochar, plus the weight of the binding agent is 100 wt% of the carbonaceous combustible of the briquettes on a dry base.

[0099] Item 37. The method of any one of the preceding items, wherein the biochar have of a particle size so that less than 20 wt% are above 16 mm, preferably so that less than 20 wt% are above 8 mm.

[0100] Item 38. The method of the preceding item, wherein the biochar have of a particle size so that less than 20 wt% are above 5 mm, preferably so that less than 20 wt% are above 3 mm.

[0101] Item 39. The method of the preceding item, wherein the biochar have of a particle size so that less than 20 wt% are above 2 mm, preferably so that less than 20 wt% are above 1 mm.

[0102] Item 40. The method of any one of the preceding items, wherein the coke or anthracite are lumps breeze of coke or are lumps breeze of anthracite, and said lumps breeze are of particle size so that less than 20 wt% are above 16 mm, preferably so that less than 20 wt% are above 8 mm.

[0103] Item 41. The method of any one of the preceding items, wherein the coke or anthracite lumps breeze are of particle size so that less than 20 wt% are above 5 mm, preferably so that less than 20 wt% are above 3 mm.

[0104] Item 42. The method of any one of the preceding items, wherein the coke or anthracite lumps breeze are of particle size so that less than 20 wt% are above 2 mm, preferably so that less than 20 wt% are above 1 mm.

[0105] Item 43. The method of any one of the preceding items, wherein the coke or anthracite lumps breeze are of particle size so that at least 30 wt% are above 2 mm, preferably so that at least 40 wt% are above 1 mm.

[0106] Item 44. The method of any preceding items, wherein the biochar is a vegetal biochar.

[0107] Item 45. The method of the preceding item, wherein the vegetal used for obtaining the biochar is selected from the group comprising: natural wood, waste wood, pruning, branches, by-products of fruit stones (such as olive stone, peach stone, walnut shell, hazelnut shell, almond shell, etc.), wood furniture wastes, wood waste in particular wood waste of class B (according to UNECE-FAO United Nations wood waste classification catalogue 2022), drinking water or waste water treatment plant muds, paper industry mud, lignocellulosic wastes, algae, phytoplankton, and combinations thereof.

[0108] Item 46. The method of any preceding items, wherein the binder comprises or is an inorganic binder selected from: Aluminum oxide (Al_2O_3), Bentonite, Calcium carbonate, Calcium hydroxide, Calcium oxide, Cement, Clays, Dolomite, Gilsonite, Glass fibers, Gypsum, Kaolin, Lime, Magnesium oxide, Alkaline silicate such as Sodium silicate or Potassium silicate, Aluminum silicate, Calcium silicate, Magnesium silicate, Solid waste of Solvay ammonia process, a Mineral filler, and mixtures thereof.

[0109] Item 47. The method of any preceding items, wherein the binder comprises at most 30 wt% or at most 25 wt% of alkaline metal silicate.

[0110] Item 48. The method of any preceding items, wherein the binder comprises or is an organic binder selected from: Acrylonitrile-Butadiene-Styrene Copolymer, Aminopolymer (Aminoplasts), Acrylic resin, Asphalt, Bitumen, Bituminous coal, Carbohydrate, Coal tar, Citric acid, Dextrin, Epoxy resin, Fat, Flour, Glyceridic oil, Fluorosilicic acid, Guar gum, Lignin, Lignosulfonic acid, Melamine-Formaldehyde polymers, Methyl cellulose, Molasse, Paraffin, Phenolic resins, Phenolic-Formaldehyde resin, Polisiloxane, Polymer resin, Polycarbonate, Polycarboxylate, Polyethylene Terephthalate, Polyolefin, Polyethylene, Polypropylene, Polystyrene, Polystyrene Copolymers, Polyvinyl acetate, Polyvinyl alcohol, Recycled Plastics, Rosin, Starch, Pre-gelatinized Starch, Sugar, Thermoplastic, Urea-Formaldehyde resin, and mixtures thereof.

[0111] Item 49. The method of any preceding items, wherein the briquette comprises 1% to 15% organic binder from item 48 list, and 1 to 12% inorganic binder from item 46 list.

[0112] Item 50. The method of any preceding items, wherein briquettes have a hot strength of at least 800°C, preferably at least 900°C, more preferably at least 1000°C (I shall include the Solvay 'Hot strength' test description in the description.

[0113] Item 51. The method of any preceding items, wherein the carbonaceous combustible comprising at least a biochar, and one or several binding agents is formed into briquettes using a compacting technique selected among: uniaxial press, roller press, extrusion, and any combination of said techniques thereof.

[0114] Item 52. The method of any preceding items, wherein the lower heating value (LHV) of the briquette is at least 26 MJ/ kg, preferably at least 28MJ/ kg, or at least 30 MJ/ kg.

[0115] Item 53. The method of any preceding items, wherein the sulfur content of the briquette is at most 1.5 wt. %, preferably at most 1.3 wt.% on dry basis.

[0116] Item 54. The method of any preceding items, wherein the biochar briquette comprises at least 80 wt.%, preferably at least 85 wt.%, or at least 87 wt.%, and even more preferably at least 92 wt% of fixed carbon on dry basis.

[0117] Item 55. The method of any preceding items, wherein the Micum Index M10 (<10 mm) is at most 20 wt. % or at most 17 wt.%.

[0118] Item 56. The method of the preceding item, wherein the Micum Index M10 (<10 mm) is at most 15 wt. % or at most 12 wt.%.

[0119] Item 57. The method of any preceding items, wherein the manufacture of sodium carbonate or sodium bicarbonate is according to the Solvay ammonia process.

[0120] Item 58. The method of any preceding items 1 to 56, wherein the manufacture of sodium carbonate or sodium bicarbonate comprises a sodium carbonate monohydrate process or a sodium sesquicarbonate process, using trona or nahcolite minerals as raw material.

[0121] Item 59. The method of any preceding items, wherein the briquette is coated with a layer comprising a compound selected among: cement, starch, limestone, and mixtures thereof.

[0122] Item 60. The method of the preceding item, wherein the weight of the layer after drying at 50°C and reported to the carbonaceous combustible weight is at least 4%, or at least 6%.

[0123] Item 61. The method of item 59 or 60, wherein the weight of the layer after drying at 50°C and reported to the carbonaceous combustible weight is at most 35%, or at most 25%.

[0124] Item 62. The method of any items 59 to 61, wherein the layer coated on the briquette is applied by mechanical deposition such as: spraying, drum or rotating pan coating, immersion coating.

[0125] Item 63. Carbonaceous combustible such as: charcoal, charcoal briquette, coke briquette, or anthracite briquette, coated with a layer comprising a compound selected among: cement, starch, limestone, and mixtures thereof, and wherein the weight of the layer after drying at 50°C and reported to the carbonaceous combustible weight is at least 4% and at most 35%.

[0126] Item 64. Carbonaceous combustible according to the preceding item, which is a briquette comprising biochar or charcoal.

[0127] Item 65. Carbonaceous combustible according to item 63, which is a coated coke briquette or a coated anthracite briquette.

[0128] Alternatively to the above embodiments, the present invention also relates to a method identical to anyone of the items 4 to 56, but wherein the amount of the binding agent(s) and the compacting pressure are adjusted so that the cold mechanical strength is not measured according to ISO 556:2020 (half drum) on briquettes of size of at least 20 mm, with a Micum Index M10 (< 10mm), but with the following shatter test:

The cold mechanical strength of the biochar briquettes of size of at least 20 mm is measured by placing 10 briquettes in a closed tube, in iron material, of internal length 1 meter and of internal diameter 65 mm, and half-rotating said cylinder in an axis placed half of his length : 200 times in 6 minutes and 40 seconds. This enable to test the mechanical strength of said briquettes falling from approximately one meter height, at each half turn. Then after the 200 half turn, the content of the cylinder is removed, the removed samples is weighed, and then is sieved on a sieve of 5 mm aperture (rather than 10 mm on the micum M10 mm test in the Iso 556 test). The size fraction under 5 mm is sieved, then weighed. And the size fraction < 5 mm mass is reported to the total sample mass recovered and weighed from the cylinder before being sieved and the result is expressed in wt.% as M5 Shatter test. The higher said M5 Shatter test index is, the weaker the biochar briquette is. The lower the M5 Shatter test index is, the better is the biochar briquette (ie with high mechanical strength).

[0129] In said alternative embodiments from Item 4 to 56 above, the values of and the references to the Micum Index M10 are replaced with the M5 Shatter test indexes values and with the M5 Shatter test index references.

Examples

Example 1

[0130] This example describes the volatile matter identification on different samples of carbonaceous combustible among metallurgical coke, hard coal anthracite, and biochar to be then shaped as briquettes.

[0131] The operating mode to identify flammable gasses freed when heated at high temperature and able to provoke explosions is described infra.

[0132] Each sample of carbonaceous combustible such as biochar or charcoal, coke or anthracite is crushed and sieved between 250 μm and 500 μm. Then according the density of the powder about 5 to 10 g of crushed coke or anthracite, or 1g to 5 g of crushed biochar or charcoal is placed in a quartz tube in U-shape, and of 20 mm internal diameter and 25 mm outside diameter, to give a fixed bed of carbonaceous combustible of about 40 mm high. The target is to quantify the mass loss during a pyrolysis of the solid fuel following a heating profile of 20°C/ minutes up to 900°C and then a plateau at 900°C during 7 minutes (similar to ISO 562:2010 standard). 100 mL/ min of nitrogen (N_2) flows through the bed, and carries out the volatiles gas to a heated line and bubblers to identify and quantify said volatiles gasses.

[0133] Both, the temperature of the oven and the temperature of the sample (inside the bed) are recorded.

[0134] At the outlet of the reactor, pyrolysis gasses are conducted via a heated line (350°C) into two consecutive bubblers filled with iso-propanol and liquid nitrogen (N_2) (about 10mL in each bubbler) and kept at 0°C and -30 °C in Dewar recipients. The permanent gasses are collected in a sampling Tedlar bag connected directly at the exit of the 2nd bubbler. The gas collected in the sampling bag is analyzed by micro gas chromatography mass spectrometer (μGC-MS) using a PPQ precolumn with a back-flush and a molecular sieve 5A for H_2, CH_4, and CO quantification. A preliminary drying of the sample is done placing the quartz-U-Tube reactor in the oven at 70°C and then set at a temperature of 110°C for 50 minutes to desorb the water. Then, the reactor is disconnected and weighted rapidly to give the mass of anhydrous solid fuel (based on the mass of the empty reactor).

[0135] The following table gives results of flammable gasses presenting an explosion risk freed when heating the different samples, in typical limekiln gas composition from sodium carbonate and bicarbonate plants:

Table 1 - Composition of flammable gasses freed when heating carbonaceous combustible up to 900°C in non-oxidizing atmosphere.

Samples	Total Volatile Matter wt%	Sum of dangerous gasses (CO + CH_4 + H_2) reported to carbonaceous combustible wt %	H_2 equivalent content regarding explosion risk wt%
Biochar resinous wood 875°C	17.2	8.6	1.70
Charcoal A	26.0	10.4	1.26
Charcoal B	16.8	9.6	1.52
Charcoal C fines 015 mm	9.0	5.1	0.85
Charcoal C Lumps 20-40 mm	8.3	4.1	1.10
Charcoal D	14.1	9.2	2.00
Charcoal Lump Hardwood E	21.2	8.4	1.27
Charcoal Hardwood E briquette + native starch	23.1	8.7	1.32
Waste wood class B carbonised 650°C	9.0	5.4	1.09
Waste wood class B carbonised 850°C	5.6	2.4	0.49
Anthracite I	3.4	1.0	0.62

(continued)

Samples	Total Volatile Matter wt%	Sum of dangerous gasses (CO + CH_4 + H_2) reported to carbonaceous combustible wt %	H_2 equivalent content regarding explosion risk wt%
Anthracite J	3.0	0.9	0.63

Example 2

[0136] The analysis of 31 samples of different biochar of different origins, and 27 samples of anthracite or metallurgical coke of different origins, gave respectively a mean value in corresponding ash content of the carbonaceous combustible:

- a mean value of 4% Si (silicon) in biochar ashes and 41% Si (ten times more) in anthracite or coke samples ashes;
- a mean value of 2.2% Al (aluminum) content in biochar ashes and 26% Al (twelve times more) in anthracite or coke samples ashes;
- a mean value of 2.5% Fe (iron) content in biochar ashes and 18% Fe (seven times more) in anthracite or coke samples ashes;

[0137] Said elements (Si, Al, Fe) present as oxides when the limestone is burnt into lime, at high temperatures, generate cementations hydraulic binders in presence of calcium hydroxides from the milk of lime when used in the ammonia distillation sector. They also increase said components in the solid residues in the effluents of the distillation sector. The use of biochar in replacement of part, or totally, of fossil carbonaceous combustible, decreases incrustations on the surface of distillation equipment. It enables also to reduce amount of solid residues in liquid effluents from the distillation sector.

Example 3

[0138] On above combustible samples, a mechanical brittleness and fragility characterization was made with the following ‘drop test’ described infra, to quantify the generation of fine particles when transporting and handling said biochar material in lumps or briquettes, compared to typical fossil solid carbonaceous combustible (such as metallurgical coke, anthracite, hard coal, etc...).

[0139] The following ‘drop test’ quantifies the average quantity of "fine particles" (< 5 mm) that will result from dropping the combustible in shape of lumps or briquettes, into a limekiln when falling on its own weight from a height of 6 meters. The quantity of fines generated under 5 mm is weighed after sieving of the tested sample.

[0140] High amount of particles less than 5 mm means that the combustible is fragile and is not recommended to be handled, transported and loaded in a limekiln.

Test description of the ’drop test’:

[0141] A suspended flexible pipe, 6 meters long, and of 20 cm internal diameter is placed vertically, dipping into a bucket to receive the falling sample to be characterized. The fallen sample, and the fines generated by the fall collected in the bucket are sieved on a sieve of 5 mm mesh. The resulting quantity of broken sample and fines generated, sieved under 5 mm, are weighed, and reported to the initial weight of the sample before the fall and expressed in weight percentage.

[0142] The measure is done on at least 3 different samples of the combustible to be characterized, preferably at least 5 different samples of briquettes, and the mean value is noted with the deviation. In case of heterogeneous combustible the number of characterized samples is enlarged to 10 samples.

[0143] On the above carbonaceous combustibles samples, said ‘drop test’ showed that :

- presently used anthracite or metallurgical coke have values of drop test which are comprised between 0.06% to 0.90% with typical mean values of 0.40 wt. %;
- briquettes comprising biochar are generally more fragile and have a spread much wider with values of drop test which are comprised between 0.20% to several weight percents. Typical mean values for biochar samples considered as compatible to be loaded in limekilns are 0.30 to 0.80%. Values above 1%, particularly above 2% should be avoided as said combustible briquette have a propensity to break easily during handling and during limekilns loading.

[0144] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

Claims

1. A method for the manufacture of sodium carbonate or sodium bicarbonate according to the Solvay ammonia process,

   wherein said method comprises a limestone calcining step in a vertical shaft limekiln, to produce lime (CaO) and a gas comprising carbon dioxide (CO_2), using a limestone and a carbonaceous combustible,
   wherein said carbonaceous combustible comprises at least partly a biochar, compacted into briquettes using one or several binding agents selected among:

   - one or several inorganic binder(s) and/ or
   - one or several organic binder(s), and

   the binding agent(s) being used in an amount expressed as the dry amount of the binding agent reported to total weight of the dry briquettes,
   wherein the binding agent(s) is(are) mixed with the carbonaceous combustible to form a mixture, the mixture is compacted at a compacting pressure in a matrix or in a screw into briquettes, the obtained briquettes are then optionally thermally cured,
   said briquettes having a particle size distribution so that:

   - at most 20% in weight of the briquettes are of size of more than 90 mm,
   - and at most 20% in weight of the briquettes are of size of less than 25 mm

   characterized in that:

   - the mass amount of the biochar reported to the briquette mass is at least 15 wt. % dry;
   - the briquettes comprises preferably at most 50 wt.% volatile matter;

     - - the amount of the binding agent(s) and the compacting pressure are adjusted so that less than 2% by weight of briquette fines under 5 mm are generated by a fall of 6 meters-high of briquettes, dropped individually and quantified as a mean value measured on a sample of at least 5 briquettes from said carbonaceous combustible.

2. The method of claim 1 wherein the biochar comprises at most 50 or at most 35 wt. % volatile matter..

3. The method of any of the preceding claims wherein the biochar comprises at least 3% or at least 4% by weight of volatile matter on a dry base.

4. The method of any one of the preceding claims, wherein the briquettes comprise at most 65 wt%, preferably at most 35 wt. % of coke or of anthracite on a dry base.

5. The method of any one of the preceding claims, wherein the briquettes comprise at least 30 wt% of biochar on a dry base.

6. The method of any one of the preceding claims, wherein the briquettes comprise at least 60 wt% of biochar on a dry base.

7. The method of any one of the preceding claims, wherein the briquettes are devoid of fossil fuel such as coke, pet coke, anthracite, lignite, or coal.

8. The method of any one of the preceding claims, wherein the briquettes comprise at most 25 wt%, or at most 20 wt% of the binding agent on a dry base.

9. The method of any one of the preceding claims, wherein the biochar have of a particle size so that less than 20 wt% are above 2 mm, preferably so that less than 20 wt% are above 1 mm.

10. The method of any preceding claims, wherein the binder comprises or is an inorganic binder selected from: Aluminum oxide (Al_2O_3), Bentonite, Calcium carbonate, Calcium hydroxide, Calcium oxide, Cement, Clays, Dolomite, Gilsonite, Glass fibers, Gypsum, Kaolin, Lime, Magnesium oxide, Alkaline silicate such as Sodium silicate or Potassium silicate, Aluminium silicate, Calcium silicate, Magnesium silicate, Solid waste of Solvay ammonia process, a Mineral filler, and mixtures thereof.

11. The method of any preceding claims, wherein the binder comprises or is an organic binder selected from: Acrylonitrile-Butadiene-Styrene Copolymer, Aminopolymer (Aminoplasts), Acrylic resin, Asphalt, Bitumen, Bituminous coal, Carbohydrate, Coal tar, Citric acid, Dextrin, Epoxy resin, Fat, Flour, Glyceridic oil, Fluorosilicic acid, Guar gum, Lignin, Lignosulfonic acid, Melamine-Formaldehyde polymers, Methyl cellulose, Molasse, Paraffin, Phenolic resins, Phenolic-Formaldehyde resin, Polisiloxane, Polymer resin, Polycarbonate, Polycarboxylate, Polyethylene Terephthalate, Polyolefin, Polyethylene, Polypropylene, Polystyrene, Polystyrene Copolymers, Polyvinyl acetate, Polyvinyl alcohol, Recycled Plastics, Rosin, Starch, Pre-gelatinized Starch, Sugar, Thermoplastic, Urea-Formaldehyde resin, and mixtures thereof.

12. The method of any preceding claims, wherein the carbonaceous combustible comprising at least a biochar, and one or several binding agents is formed into briquettes using a compacting technique selected among: uniaxial press, roller press, extrusion, and any combination of said techniques thereof.

13. The method of any preceding claims, wherein the vegetal used for obtaining the biochar is selected from the group comprising: natural wood, waste wood, pruning, branches, by-products of fruit stones (such as olive stone, peach stone, walnut shell, hazelnut shell, almond shell, etc.), wood furniture wastes, wood waste in particular wood waste of class B (according to UNECE-FAO United Nations wood waste classification catalogue 2022), drinking water or waste water treatment plant muds, paper industry mud, lignocellulosic wastes, algae, phytoplankton, and combinations thereof.

14. The method of any preceding items, wherein the briquette is coated with a layer comprising a compound selected among: cement, starch, limestone, and mixtures thereof.

15. The method of the preceding claim, wherein the weight of the layer after drying at 50°C and reported to the carbonaceous combustible weight is at least 4%, and at most 25%.

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EUROPEAN SEARCH REPORT

Application Number
EP 23 21 9660

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	FLORENTINO-MADIEDO L ET AL: "Mechanical strength of bio-coke from briquettes", RENEWABLE ENERGY, PERGAMON PRESS, OXFORD, GB, vol. 146, 1 August 2019 (2019-08-01), pages 1717-1724, XP085904555, ISSN: 0960-1481, DOI: 10.1016/J.RENENE.2019.07.139 [retrieved on 2019-08-01] * abstract * -----	1-15	INV. C01D7/12 C01D7/18 C01F11/06 C10L5/02 C10L5/10 C10L5/32 C10L5/36 C10L5/44
A	SUOPAJÄRVI HANNU ET AL: "Extensive review of the opportunities to use biomass-based fuels in iron and steelmaking processes", JOURNAL OF CLEANER PRODUCTION, ELSEVIER, AMSTERDAM, NL, vol. 148, 7 February 2017 (2017-02-07), pages 709-734, XP029939583, ISSN: 0959-6526, DOI: 10.1016/J.JCLEPRO.2017.02.029 * abstract * -----	1-15	
			TECHNICAL FIELDS SEARCHED (IPC)
A	EP 2 883 943 A1 (ARIGNA FUELS LTD [IE]) 17 June 2015 (2015-06-17) * claims * -----	1-15	C01D C01F C10L
A	WO 2022/271032 A1 (BIOCARBON SOLUTION AS [NO]) 29 December 2022 (2022-12-29) * page 3, line 32 - page 4, line 15 * * claims * -----	1-15	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	13 May 2024	Keipert, Olaf

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 23 21 9660

13-05-2024

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EP 2883943 A1	17-06-2015	NONE	
WO 2022271032 A1	29-12-2022	NONE	

EPO FORM P0459

REFERENCES CITED IN THE DESCRIPTION

Non-patent literature cited in the description

- Ullmann’s Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co, 2002, 24 **[0016]**
- *European Union - IPPC BAT Reference Document - Process BREF for Soda Ash manufacturing*, March 2004 (3), 30 **[0024]**