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(54) Title: USE OF TORREFACTION CONDENSATE

(57) Abstract: The product obtained by condensation of organic material volatilised during torrefaction of biomass can be used as a binding agent or coating agent or additive for solid carbonaceous material to produce wear-and water-resistant solid fuel, which can be largely or entirely derived from biomass. The resulting product is suitable as a (partially) renewable solid fuel.



Use of torrefaction condensate

Field of the invention

[0001] The invention is in the field of torrefaction of biomass. The invention is also in the field of producing solid fuels as well as chemicals and materials.

5 Background of the invention

[0002] Torrefaction is a technique for producing valuable materials such as fuel, from wood or biomass waste such as plant residues from agriculture or silviculture. Torrefaction is a thermal treatment at moderate temperatures in the substantial absence of oxygen. Torrefaction is distinguished from pyrolysis by the temperatures used: while
10 pyrolysis employs temperatures of 300-700°C, in particular 400-500°C, the temperatures used in torrefaction are between 200 and 350°C.

[0003] A method for torrefaction of biomass, wherein the biomass is first dried in a co-current mode and is then torrefied in counter-current operation, is described in WO 2007/078199.

15 [0004] US 2010/0083530 (CA 2681282) discloses a torrefaction process wherein wet cellulose material is cascaded down a torrefaction reactor to produce steam and volatiles, in addition to a dried solid. The volatiles can be used for their calorific value.

[0005] Commonly, torrefied fuel is densified. It is done for several reasons. Primarily, it improves logistics (transport and storage), but it also leads to efficient
20 feeding in combustion and gasification installations. Densification is done by mechanical compression, e.g. pelleting, briquetting and tableting. In densification, binder may be added to improve the cohesion of the material and the resistance against wear or breakage. The binder also acts as a lubricant in the compression, lowering energy consumption of the machine and diminishing porosity, thus increasing density.

25 [0006] The use of torrefied biomass as a substitute for fossil fuels, such as coal, is hampered by the fact that the currently used binders are expensive and undesired from a sustainability point of view or result in products that have low strength and cannot easily be processed to pellets and briquettes.

Summary of the invention

30 [0007] It was found according to the invention, that the volatile organic fraction of a biomass torrefaction process, after condensation, is excellently suitable for binding and/or coating solid biomass and other carbonaceous material, resulting in high-calorific-value and wear and water resistant, shippable solid fuel.

[0008] Hence, the invention pertains to the use of a biomass torrefaction condensate (BTC) as a binding agent or coating agent for solid material, as well as to its use as either bio-based chemical or material or bio-based additive to chemical or material. The invention furthermore pertains to a process for producing a wear- and water-resistant solid fuel, comprising combining a solid carbonaceous material with a BTC obtained by condensation of organic material volatilised during torrefaction of biomass. In one embodiment, the solid material is biomass-derived, such as torrefied biomass.

[0009] The invention in particular concerns a process for upgrading biomass comprising:

- a. subjecting the biomass to torrefaction, to produce a torrefied solid fraction and a volatilised fraction;
- b. cooling the volatilised fraction to produce an organic condensate;
- c. combining the condensate of step (b) with a torrefied solid fraction, of step (a) or of another process;
- d. densifying the torrefied solid fraction of step (a) (prior to step (a)) or step (c) (after step (c)).

Where step (d) precedes step (c), step (c) preferably comprises coating the torrefied solid fraction of step (d). A further step may comprise tuning and/or upgrading the condensate of step (b).

[0010] Furthermore, the invention pertains to the (partially) biomass-derived products including solid fuel obtainable by these processes.

Description of the invention

[0011] The invention concerns the use of a biomass torrefaction condensate as a binding agent or coating agent or other additive for solid biomass-derived material. The term "biomass torrefaction condensate" (BTC) is used herein to denote a condensate which can be obtained by conducting a part of the exhaust gas of a biomass torrefaction process, as further described below, containing organic volatiles and water, through a condenser and collecting organic condensate, and optionally water.

[0012] Alternatively, although somewhat less preferred, the BTC can also be used as a binding agent or coating agent or other additive for other materials such as fly ash, char and/or charcoal, although not limited thereto. According to yet a further aspect, the BTC is a suitable biobased feedstock for or additive to a wide range of chemicals and materials. This includes for example bio-bitumen, and resins, which can be used as

additives, e.g. adhesives, fillers, binders, in products like pavings, floorings (e.g. linoleum), or construction materials such as chipboard, together with oils, cork, wood dust, wood chips, other organic or inorganic fillers etc. or in paints, protective coatings, inks and the like, as lubricants, etc.. The BTC can also be used as phenol substitutes in wood resins (phenol-formaldehyde resins) or as a substitute for high value phenolic compounds like guiacols, syringols and alkylated phenols. The BTC can be present as a final product as well as a fraction in the final products at a level of between 0.5 and 50 wt.%, preferably 1-25 wt.%, most preferably 2-12 wt.%, especially in shaped products such as sheets, plates, tiles, bricks, etc., in addition to 5-95 wt.%, preferably 20-90 wt.% of one or more of oils, cork, wood dust, wood chips, other organic or inorganic fillers etc.

[0013] The properties of the BTC as an additive (binder, filler, adhesive, lubricant, etc.) can be tuned by adjusting the material and parameters: types of starting biomass (e.g. coniferous wood or deciduous wood, straw or other agricultural residues, mixtures thereof), degree of pre-drying, torrefaction temperatures, torgas cycle ratio, cooling temperatures, etc. Alternatively, the BTC can be upgraded (e.g. by extraction or distillation).

[0014] It is preferred that the BTC is condensed at a temperature which is between 100°C above and 50°C below the condensation temperature of water, preferably between 90°C above and 20°C below the condensation temperature of water, more preferably between 80°C above and 10°C below the condensation temperature of water, most preferably between 60°C above and the condensation temperature of water. When cooling the torrefaction exhaust gas, the temperatures and pressure are selected in such a manner that, depending on the content of water and organic molecules in the gas, most of the organic material is condensed, while most, but not necessarily all water remains in the vapour phase.

[0015] The BTC itself preferably comprises all material which is condensable between the torrefaction temperature (200-350°C, especially 240-320°C, see below) and 50°C below the condensation temperature of water, most preferably between the torrefaction temperature and the condensation temperature of water (e.g. 100°C at atmospheric conditions). The heavier components of the BTC, i.e. the components which are condensed first, were found to be highly valuable in the use according to the invention. The BTC is a multi-component material comprising lignin degradation

products and other biomass-derived organic molecules. Their molecular weights will be broadly in the range of 30-220 Da, in particular 60-170 Da. The BTC contains at least 5 wt.%, up to 70 wt.%, in particular between 10 and 40 wt.% of phenolic compounds, in particular having the formula $R^1R^2C_6H_3OH$, wherein R^1 is methoxy, ethoxy or C_1 - C_3 alkyl or alkenyl, and R^2 is hydrogen, hydroxyl or methoxy. The BTC has a condensation temperature range between below the condensation temperature of water up to the torrefaction temperature, e.g. at atmospheric pressure 50-350 °C, preferably 100-320°C. The fraction which has a condensation temperature range (boiling point range) between 150 and 300°C is most valuable. On the other hand, a proportion of the BTC preferably is low-boiling, i.e. having a boiling range between 65 and 150°C. If necessary, diluents such as alcohols (ethanol, butanol) or aromatics, such as toluene and xylenes, or other moderately polar and inoffensive solvents can be used to provide the BTC with the required viscosity so as allow convenient processing, e.g. at a level of between 3 and 30 wt.% of the (dry) BTC.

[0016] The BTC may comprise up to 80 wt% water, but preferably less, e.g. below 50 wt.%. The water content may vary depending on the temperature at which the BTC is condensed. Where necessary to lower the water content of the agent, the temperature at which the BTC is condensed may be between 0°C and 100°C above the condensation temperature of water, in particular between 5°C and 80°C above the condensation temperature of water. Alternatively, further cooling and separation of water may be used. On the other hand, where the water content is too low, water may be added before using the condensate as a binding or coating agent. The amount of water can e.g. be 0.25-2.5 times the amount of (dry) condensate, preferably 0.4-1 times the amount of (dry) condensate. Water may also be added separately, directly to the densification process, for example directly into the pelletisation apparatus. Water may be added as liquid or as vapour.

[0017] If necessary, the BTC binding or coating agent may contain further additives, which enhance the processability or homogeneity of the agent. Such further additives may include organic solvents, such as alcohols (e.g. ethanol, butanol), glycols (ethylene glycol propylene glycol), or higher polyols such as glycerol. However, the use of such further additives is not always necessary, and if used, their level is preferably below 50 wt.% based on the total weight of the agent, in particular between 0 and 20 wt.% thereof. Also if used, such additives may preferably be low-grade, i.e.

contain water or further organic components, preferably excluding heteroatoms such as sulphur, halogens, metals etc.

[0018] When used as a binding or coating agent, the BTC is advantageously used in a weight ratio of below 1:3 (= <25%), especially a weight ratio of below 1:4
5 (= <20%), down to e.g. 1:199 (0.5 wt.%). When used as a binding agent, it is preferably used at between 1:99 and 1:7 (1-12.5%), more preferably 1:99 to 1:9 (1-10%) to the solid material. When used as a coating agent, the ratio is preferably between 1:24 and 1:4, while ratios between 1:19 and 1:7 are preferred.

[0019] Any solid or solid-like biomass or other (semi) solid carbonaceous material
10 as defined below, having insufficient resistance to dusting or rupture or having insufficient wear- and/or water resistance, may be treated with the BTC as a binding or coating agent. Examples include wood dust, wood chips, as such or in compressed form, agricultural waste etc. The biomass may be treated as such. Particularly useful is a solid biomass-derived material which is thermally pre-treated so as to increase its
15 value as a biomass-derived fuel, most in particular by torrefaction of the biomass. As a result of the thermal pre-treatment, the biomass has lost part or most of the effectiveness of its natural binding agents, such as lignin and/or resin. In this way two components from the same process are efficiently used, i.e. the torrefied solid mass as the basic biomass material and the condensed volatiles (BTC) as the binder or coating
20 agent. Besides torrefied biomass, other carbonaceous material with insufficient intrinsic binding agents, such as fly ash, char or charcoal, can also be advantageously treated according to the invention.

[0020] The term "biomass" as used herein denotes organic material derived from plant in any form, in particular wood, straw and other plant residues and the like. For
25 the purpose of this invention, biomass also encompasses peat, manure, recycled wood, as well as algae and seaweeds. A "carbonaceous material" is any material which contains substantial amounts, specifically at least 10 wt.%, in particular at least 25 wt.%, of carbon, wherein fully oxidised carbon (i.e. in carbon dioxide or carbonate form) is excluded. In particular, carbonaceous material encompasses biomass and fossil
30 carbon-containing materials such as coal, oil residues and other non or incompletely combusted (solid) combustibles.

[0021] Also for the torrefied material and condensate, this may originate from any type of biomass as described above. Particularly useful is a biomass which consists partly or largely, say at least 50 wt% (dry weight basis), of wood, herbaceous plants,

agricultural (plant) residues or combinations thereof. Preferably at least 70 wt% consists of biomass-derived material, in particular of wood and or herbaceous plants, most preferably at least 50 wt% of wood. The wood may be hard wood (deciduous) or soft wood (coniferous) or any mixture thereof. Any remaining part of the biomass may originate from straw or other agricultural or silvicultural waste, or other organic waste having acceptable levels of hazardous contaminants such as halogen compounds, and the like. Non-biomass, i.e. fossil derived organic material may be admixed, but preferably at minor levels, e.g. below 25 wt.% only.

[0022] In another aspect, the invention concerns a process for producing a wear- and water-resistant solid biomass-derived fuel, comprising combining a solid biomass-derived material with a BTC as described above. The content of BTC may be between 1 and 25 wt.%, based on the weight of the final product.

[0023] When the BTC is used as a binder, it can be mixed with the solid biomass in the described ratios. The precise ratio can be determined by the skilled person as a function of the further processing steps and the ultimate use of the solid material. Likewise, the precise water level can be adjusted so as to achieve optimum results. Mixing can be done separately, in a distinct mixing equipment, or it can be part of the further densification steps, such as pelleting, briquetting or tableting.

[0024] The invention also applies to torrefied or heat-treated biomass that undergoes densification. In particular it is of use in pelletisation and briquetting as described below. The invention may also be applied to tableting or any other form of densification. Pelletisation can be carried out in conventional pelletising equipment such as used for producing wood pellets from chips or animal feed pellets. The binding agent may be directly fed into the pelletiser or prior to entering the pelletiser. In a particular embodiment, the BTC is produced *in situ*, i.e. the gas flow, or part of it, containing the organic volatiles of the torrefaction process, is brought in contact with the solid (torrefied) biomass at relatively low temperatures, resulting in condensation of the organic volatiles onto the solid biomass. Thus, in a preferred process according to the invention, the organic material volatilised during torrefaction of biomass is directly condensed onto the solid biomass-derived material. The temperature of the torrefied biomass being subjected to the stream of organic volatiles is chosen as described above for the temperature at which the BTC is condensed, and can be varied depending on the desired amount of water condensation onto the torrefied biomass. Thus, the biomass which is subjected to the stream of organic volatiles is between 100°C above and 50°C

below the condensation temperature of water, especially between 90°C above and 20°C below, preferably between 80°C above and 10°C below the condensation temperature of water, most preferably between 60°C above and the condensation temperature of water.

5 **[0025]** Briquetting is another form of densification to be used according to the invention. For briquetting, material is enclosed in a space and subsequently force is applied from one direction or more directions. Briquettes are larger than pellets, typically more than 20 mm in diameter. The energy needed to make them is much lower than for pelleting. Typically, briquetting is done cold or with heat applied from
10 outside, while in pelleting the material is heated up substantially as a result of the friction in the die. At least three forms of briquetting can be distinguished: i) between two rolls with hemispherical spaces, ii) by compressing in a cycle where the previous briquette is immovably clamped at the exit acting as a temporary fixed wall; iii) extrusion of a single strand, similar to pelleting but with a much larger diameter; the
15 strand is cut into briquettes. In the latter two forms, the force can be generated hydraulically, from a fly wheel with an eccentrically mounted piston or a feeder screw. The way BTC is used in briquetting is analogous to its use in pelletisation (see above).

[0026] When the BTC is used as a coating agent, it is applied onto the solid biomass material after densification using conventional coating technique such as
20 spray-coating, dip-coating etc. The precise amounts of coating agent are determined on the basis of routine adjustment depending on the shape and further characteristics of and requirements for the final material. When the BTC is used as a bio-based chemical such as bitumen, or resin, for use as a binder, filler, adhesive, lubricant, or the like, it can be combined with other materials such as wood dust or chips, cork, cements, other
25 resins etc., in a manner known per se for conventional binders, fillers, adhesives etc.

[0027] The invention further encompasses a process for upgrading biomass comprising:

- a. subjecting the biomass to torrefaction, to produce a torrefied solid fraction and a volatized fraction;
- 30 b. cooling the volatized fraction to produce an organic condensate;
- c. combining the condensate with torrefied solid fraction;
- d. densifying the torrefied solid fraction, either after, before or during combining with the condensate in step (c); when the condensate is used as a binder for the

torrefied solid fraction, combining (i.e. mixing) takes place before or during densification, and when the condensate is used as a coating agent for the torrefied solid fraction, combining (i.e. coating) takes place after densification.

[0028] The torrefaction is performed at a temperature of between 200 and 350°C, preferably between 240 and 350°C, more preferably between 240 and 320°C. Upon combining both fractions in step (c) the weight ratio between said organic condensate and said torrefied solid fraction is preferably between 1:4 and 1:99.

[0029] In an advantageous embodiment, no more than 10 wt.%, of other additives than an organic torrefaction condensate is used on the basis of the dry weight of the torrefied mass fraction, preferably less than 5 wt.%. Such less desired additives include starch and other materials that would have to be abstracted from potential food supplies, and fossil-derived polymers and derivatives. If used, they are used at a level of no more than 50 wt.% of the BTC. An acceptable further additive, which may be used up to e.g. 20% of the dry weight of the torrefied mass, or up to 50wt.% of the BTC, may be lignin obtained from wood in another way than as a torrefaction condensate.

[0030] The invention also pertains to a torrefied biomass-derived material, suitable as a fuel, obtainable by the process as described herein. Such a biomass-derived fuel can be defined by one or more of the following characteristics:

- i. an outer particle size of between 2 mm and 10 cm as smallest diameter;
- ii. a bulk density of between 0.35 and 1.0 kg/dm³, preferably between 0.65 and 0.9 kg/dm³;
- iii. a specific density between 0.8 and 1.5 kg/dm³, preferably between 1.1 and 1.4 kg/dm³;
- iv. a calorific value on dry and ash-free basis of between 15 and 28 MJ/kg especially a higher heat value (HHV, taking into account the vapour energy of water) of between 18 and 28 MJ/kg, preferably between 21 and 25, and/or a lower heat value (LHV) between 18 and 23 MJ/kg;
- v. a moisture content of less than 5 wt.%, also after storage at ambient conditions for at least 1 month;
- vi. a carbon content derived from biomass of at least 75%, which can for example be determined by its ¹⁴C content of at least 5.10⁻¹³ (0.5 ppt) on carbon basis;
- vii. a grindability which is comparable to the grindability of coal, corresponding to a power consumption below 0.5 MJ/ton on a 0.25 mm mesh;

viii. stability to ambient (outdoor) conditions for at least 1 month.

[0031] For the stability test, analyses are typically performed by exposing a 1 kg-sized sample to a set humidity level (working range 0-95 %, typically in the range of 70-95 % relative humidity) at a desired temperature (range -40 to +80 °C, typically 5-
5 25 °C) over a desired period of time (typically 7 days, though which can be extended to 1 month) in a climate chamber sufficiently large to accommodate several specimens. Samples are drawn after specific time intervals during the period of exposure. The moisture uptake investigations are aided by standard moisture analyses. A visual observation of mold formation or other signs of biologic degradation (discoloration,
10 effluent or gas formation) is also done to check stability. Another rapid test for sufficient stability consists in submerging particles (e.g. pellets) in water of ambient temperature for at least 24 h, in particular 1 week; if the particles can be taken from the water without noticeable softening or other visible change, the stability is rated to be sufficient.

15 **[0032]** A solid fuel produced according to this invention may be made from torrefied biomass and BTC, with less than 5 wt% of other additives present, preferably less than 2 wt%, in particular less than 0.5 wt%. In this embodiment, the biomass and the binder, and optionally even a part of the water or the entire water fraction, which are used in the densification process, all originate from the biomass which was fed to
20 the torrefaction reaction, and thus less waste is produced. Hence, solid fuels produced according to the invention and a densification process according to the invention are more energy and waste efficient than prior art pellets and processes.

[0033] BTC has improved properties as a binder compared to pyrolysis oil. In general, pyrolysis oil is more acidic than BTC, contains more water and it also does not
25 harden when cooled or tempered. Pyrolysis is performed at higher temperatures than torrefaction, and the condensate of the pyrolysis gas (pyrolysis oil) comprises smaller molecules, i.e. the lignin and hemicelluloses components of the biomass are degraded into smaller molecules, because of the high pyrolysis temperature. This degradation into smaller molecules comprises hydrolysis or decomposition of lignin and hemi-
30 cellulose derivatives, thereby producing phenolic and carboxylic acid moieties and molecules. These moieties render pyrolysis oil more acidic than BTC, and enable more hydrogen bridges to be formed with water, which results in a higher water content of pyrolysis oil compared to BTC. Using BTC as a binder, pelletising is possible at typical temperatures in a pellet mill, around 140°C, retaining its binding characteristics, which

results in hard pellets. Furthermore, in case of pyrolysis oil, the higher acidity causes gas formation during pelletisation at elevated temperatures, which induces foaming of the pellet. Pellets resulting from biomass pelletisation with pyrolysis oil as binder are of low quality, i.e. have a lower hardness and are less wear and water resistant than pellets obtained with BTC as binder.

[0034] Torrefaction at elevated temperatures, such as above 240°C, preferably above 260°C, causes more lignin to break down into smaller molecules, which evaporate into the gas phase. The resulting torrefied biomass has a higher calorific value and a higher carbon content than biomass torrefied at lower temperatures, due to this heat treatment. This biomass resembles charcoal more than low-temperature torrefied biomass. However, densifying torrefied biomass obtained by torrefaction at elevated temperature used to be more problematic, as a result of the lower effectiveness of the lignin residues remaining in the torrefied biomass acting as a binder. Hence, after torrefaction at elevated temperatures addition of more binder is needed for easy densification, resulting in more additives in the final pellet. Addition of BTC as a binder solves this problem, as BTC originates from the same biomass as the torrefied biomass, which is now low in lignin residues. Hence, no other additives are needed for processing, including pelletising or briquetting of the torrefied biomass, resulting in a solid fuel with a very low, if any, content of material which does not originate from the biomass that was fed to the torrefaction chamber.

[0035] The pellet or briquette according to the invention preferably comprises at most 5 wt% other additives, preferably at most 2 wt% in particular at most 0.5 wt%. Herein, other additives that are not present in the solid fuel or in very small amounts comprise materials that are potentially suitable as food components such as starch, fossil derived components, but also although with less drawbacks, minerals such as cement, clay, etc.. In a most preferred embodiment, the solid fuel contains at least 99.5 wt% material that originates from biomass, in particular from a biomass torrefaction process.

[0036] The torrefaction process can be carried out as described below. The organic material may for instance have a moisture content of 5-15%. The organic material with the residual moisture is introduced into the torrefaction reactor. The material is heated in the substantial absence of oxygen, usually though not necessarily under atmospheric pressure, to a temperature of 200-350 °C, preferably 240-320 °C, more preferably 250-310 °C, for example 260-300 °C. Torrefaction may begin as soon as the temperature of

the material exceeds about 200 °C. The lack of oxygen prevents the material from burning. Instead the material is torrefied, which leads to loss of mass because of the elimination of gases. This loss of mass generally amounts to about 10-50%, typically around 30%, while the energy value is only reduced by 5-20%, typically 10%. In
5 general, the torrefying chamber is flushed with a gas substantially free of oxygen, such as a CO₂, N₂ steam and/or recirculated process gasses. Preferably, the water content of the organic material provides the majority of the process gas, so that supply of additional process can be avoided. The torrefying chamber, but also the gas transport structure may be kept at a pressure in the range of -0.5 to +20 bar, and in general at a
10 pressure near atmospheric pressure.

[0037] The gas issuing from the torrefaction reactor is conducted through a cooling chamber downstream from the torrefying chamber gas outlet, to allow condensables to be condensed from the gas, for example in the cooling chamber, to produce the biomass torrefaction condensate (BTC). When a gas recycle system is applied, the remaining
15 gas thus obtained from the cooling chamber may then be heated again in a heating chamber to reach a temperature suitable for introduction into the torrefying chamber. Cooling may comprise cooling to a cooling temperature in the range of higher than about 50°C below the dew point of water and lower than the torrefying temperature in the torrefying chamber. In general, the cooling temperature will be around or above the
20 condensation temperature of water, and preferably below about 200 °C. For instance, the cooling temperature may be selected from the range of 90-180 °C, such as about 110-140 °C; this may especially apply at atmospheric conditions. At pressurised conditions, the selected temperature may be correspondingly higher. Alternatively, but less preferred, the cooling may comprise cooling to a cooling temperature in the range
25 of about 20°C below the boiling point of water and lower than the torrefying temperature in the torrefying chamber. In general, the cooling temperature will be around or above the boiling point of water, and preferably below about 200 °C. The cooling chamber may comprise a receiver, arranged to receive liquid from the cooling chamber and optionally arranged to receive liquid from the heating chamber. This
30 receiver can be to receive the BTC, which is condensed from the gas issuing from the torrefaction process (= "torgas"). The receiver may act as a gas liquid separating device separating liquid droplets and/or aerosols from the gas stream. The receiver may further be connected with a storage vessel.

[0038] The condensate (BTC), mainly originating from the lignin fraction in the biomass, is used as a binder in the production of biomass-derived fuels. The BTC has a calorific value significantly higher than the original feedstock, typically between 28 and 35 MJ/kg on a dry basis, and an elemental composition similar to the elemental composition of lignins. It has a high solubility in ethanol or glycerol and less high solubility in water or hydrocarbon liquids such as diesel. Evaporation of the condensate is only possible without substantial carbonaceous remainder, if it is in the form of aerosols below about 1 micron in diameter. The condensate is not stable at elevated temperatures. For atmospheric conditions, at 100 °C mass loss of around 15 % may occur over a week. At temperatures exceeding 200 °C the condensate may rapidly degrade leaving a carbonaceous residue behind, unless the condensate liquid is in the form of aerosols.

[0039] When quantities above a few gram are heated to a temperature that causes rapid degradation, gases that are released cannot readily escape the degrading liquid and blow it up into a foam resulting in a very low density char, that is a density below 50 g/l and sometimes below 20 g/l. The PAH (polyaromatic hydrocarbons) content of the condensate is typically below 1 ppm and therefore significantly lower than for condensate products rich in lignin fragments from slow or fast pyrolysis processes known. The viscosity of condensate that has not been significantly degraded approaches that of water at a temperature of 100 °C and is comparable to honey in the temperature range 0 to 40 °C.

[0040] A torrefying device to be used according to the invention may comprise:

- a. a torrefying chamber configured to torrefy organic material, the torrefying chamber further comprising a torrefying chamber gas inlet for a gas and a torrefying chamber gas outlet for removal of torrefying chamber gas from the torrefying chamber;
- b. a gas transport structure, downstream of the torrefying chamber gas outlet, comprising a cooling chamber, comprising a cooling chamber opening for the separation of BTC, and downstream from the cooling chamber optionally a heating chamber;
- c. optionally a gas transport device configured to remove torrefying chamber gas via the torrefying chamber gas outlet from the torrefying chamber and configured to transport torrefying chamber gas through the gas transport structure (at least through the cooling chamber and optionally also through the heating chamber).

[0041] The liquid material obtained after cooling is used according to the invention as described above and illustrated below. Also the remaining gas may be used. As indicated above, it may partly be reused, and introduced (after heating) to the torrefying chamber, and produced torgas may partly be taken from the loop and combusted in a combustor to provide energy for the system. The torrefying device may further comprise an additional gas source, configured to provide torrefying gas into the torrefying chamber.

Examples

10 *Example 1*

In order to investigate the BTC in detail, a 50-100 kg/hr plant was operated to study the role and fate of organic components and the behaviour of these organic components during cooling of the torgas. As long as the temperature of the wall is cooler than the torgas temperature and above 50 °C, the condensate is fluid, not sticky, and easily removed. As long as the temperature of the wall is cooler than the torgas temperature and above the water dew point of the gas – at atmospheric conditions almost 100°C – the condensate is fluid, non-sticky, and easily removed and will contain limited amounts of water. The absence of water in the BTC for the utilization of the BTC as a binder however is not crucial.

20 The amount of BTC produced depends on the feedstock, the cooling temperature in the torgas loop, but more importantly also on the operating temperature of the torrefaction process. When the torrefaction temperature is increased, more volatile organic components will be released, providing a different ratio of BTC versus torrefied biomass. At 235°C, the amount of BTC related to the torrefied biomass will be low, in a typical experiment as presented in the table below 0.3%. When increasing the temperature of torrefaction to 245 and 255°C, this amount increases to 2.3 and 4.0%, respectively. Indicative trials at higher temperatures show that percentages above 10% can also be obtained. The results are presented in Table 1.

**Table 1: Mass balance of test with wood chips
at stable periods at three temperature setpoints
(wood chips, moisture content 18.9 % as received)**

	235°C	245°C	255°C
Input			
Wet biomass amount (kg) (accuracy = ± 20 kg)	714	1311	1423
Wet biomass rate (kg/h) (accuracy = ± 0.5 kg/h)	55.1	56.3	53.8
Dry biomass amount (kg) (accuracy = ± 20 kg)	579	1063	1154
Dry biomass rate (kg/h) (accuracy = ± 0.5 kg/h)	44.7	45.7	43.7
Output			
Torrefied biomass amount (kg) (accuracy = ± 20 kg)	559	909	941
Torrefied biomass rate (kg/h) (accuracy = ± 0.5 kg/h)	43.1	39.1	35.6
Solid yield on dry biomass basis (%)	96.5	85.5	81.5
Torgas amount (without biomass moisture) (kg)	20.6	154	213
Torgas rate (without biomass moisture) (kg/hr)	1.6	6.6	8.1
Gas yield on dry biomass basis (%)	3.5	14.5	18.5
BTC amount (kg)	1.5	21.2	37.3
BTC rate (kg/hr)	0.25	0.91	1.4
BTC yield on torrefied biomass basis (%)	0.3	2.3	4.0

5 Example 2

BTC extracted from torrefaction of poplar chips was used as a binder as follows:

2.83 kg BTC was mixed with 1.12 kg ethanol at ambient temperature to produce a 72 % solution. The liquid was a thick dark fluid. 50 ml of this mixture was added to 2.5 kg of solid material torrefied at 265°C. Effectively, the batch contained 1.4 wt% BTC on the torrefied material. The batch was left for several hours. A reference batch was prepared by adding 20 gram water to 400 gram solid material. The total moisture

content was about 11 wt%, which was found to be suitable for making pellets in previous tests.

The tests were performed in a pelletising machine with a die of 4.8 mm. The reference material was used for flushing the machine. When continuously running, the input was switched to material with added BTC. The output data are presented in Table 2.

Table 2

	with BTC	with water
moisture in material [wt%]	5.72	5.72
added water [wt%]	-	5.0
added BTC [wt%]	1.4	-
pellet moisture (end product) [wt%]	3.7	not determined
pellet density (material) [kg/m ³]	1151	1104

Running the process with added BTC results in significant changes:

- less noise in pelletisation
- significantly less power consumption
- less wear of the machine
- longer pellets
- less dust.

Thus both pellet and operation quality improve, the latter specifically due to the lubricating nature of the condensate. The lowering of the power consumption for pelleting is of particular interest.

The specific density of pellets with BTC was found to be higher, but it can be regarded as being the same as without addition of BTC, 1104 and 1151, respectively, since this is within the variation found in individual pellets.

Ethanol was added only to facilitate mixing of the BTC and was evaporated during pelleting. When operating at elevated temperatures, the BTC is sufficiently fluid to be blended without ethanol.

Conclusion of this test

The use of BTC as a supplement to torrefied material is a significant improvement, with several technical advantages and no apparent disadvantages.

Example 3

The binding effect of the BTC as function of the torrefaction temperature as well as residence time at which it is extracted, were investigated by torrefying birch wood

chips at 240, 255 and 270 °C. This led to the produced amounts as mentioned in table 3.

Table 3

	Torrefied wood produced (kg/hr)	BTC produced (kg/hr)	Fraction BTC in total product (wt.%)
Birch 240°C	35.3	0.8	2.2
Birch 255°C	34.3	1.8	5.0
Birch 270°C	33.1	2.8	7.9

- 5 The torrefied wood and the condensates were used to produce pellets using a single pellet Pronto press. The amounts of condensate applied were varied according to a ratio of condensate to torrefied wood of 2.5, 5.0 and 7.5 wt.%. Hence, for the birch wood torrefied at 240°C it was attempted to add almost the same ratio of BTC produced (2.5% vs. 2.2% produced) as well as significantly more (7.5%), whereas for the birch
- 10 wood torrefied at 270°C it was attempted to add almost the same ratio of BTC produced (7.5% vs. 7.9% produced) as well as significantly less (2.5%).

Table 4 summarises the pellet density in kg/m³ after pelletisation at 160°C. Higher density indicates lower porosity and higher strength. When marked with an x, good

15 pelletisation was not possible. Pelletisation was performed at lower temperatures as well (60, 80, 100, 120 and 140°C) showing all the same result, whereas higher torrefaction temperatures lead to lower densities, adding BTC as binder can increase the density again. However, there seems to be a limit to the amount of BTC that can be applied, which is temperature dependent and corresponds closely to the amount of BTC

20 actually produced during torrefaction. When adding more BTC, the BTC is pressed out of the pellet and the pellet becomes sweaty.

Table 4

	No BTC	2.5% BTC	5.0% BTC	7.5% BTC
Birch 240°C	1268	1323	x	x
Birch 255°C	1221	1268	1294	x
Birch 270°C	1173	1234	1251	1261

At torrefaction temperatures of 240 to 270°C this can be explained by the fact that part

25 of the lignin that forms the basis of the BTC is still present in the torrefied wood chip

as it is not evaporated or degraded. The lignin that remained in the chip together with the BTC forms the binding agent, apparently limited to a certain ratio of BTC that can be added.

5 *Conclusion of this test*

The use of BTC as a supplement to torrefied material is a significant improvement, with the BTC produced at different torrefaction temperatures being applicable in the full amount produced.

General conclusions

- 10 An organic binder such as BTC is often needed for producing a solid biomass-derived fuel (e.g. as a coal substitute) of desired quality (Example 2). At torrefaction temperatures below 240°C, product qualities cause the torrefied solid to be less suitable as a solid fuel in terms of processability (grindability etc.), stability and caloric value, even with use of a binder. Moreover, the amount of BTC produced at lower
- 15 temperatures is not sufficient to achieve optimum performance after binding when using the same BTC as a binder (Example 1).
- Amounts of BTC produced, but also amounts of non-condensed gas, are proportional to the torrefaction temperature, at least over the range of 235-300°C (Example 1), while density of the solid material decreases (Example 3). At the same time the composition
- 20 of the BTC changes with increasing temperature, while at temperatures above about 300°C, and more seriously at temperatures above 350°C binding capabilities will decrease because of excessive degradation of lignin. Amounts of BTC that can be incorporated as a binder into solid material resulting from torrefaction increases with temperature, and the binder increases the density and strength of the solid material
- 25 (Example 1).

Claims

1. Use of a biomass torrefaction condensate (BTC), obtained by torrefying biomass at a temperature of between 240 and 350°C and condensing the volatized fraction of the torrefied biomass at a temperature which is between 100°C above and 50°C below the condensation temperature of water, as a binding agent for solid material.
2. Use according to claim 1, wherein the BTC has been condensed at a temperature which is between 80°C above and 10°C below the condensation temperature of water, most preferably between 60°C above and the condensation temperature of water.
3. Use according to claim 1 or 2, wherein the BTC has a condensation temperature between 100°C and the torrefaction temperature.
4. Use according to any of claims 1-3, wherein the binding or coating agent is used in an amount of between 1 and 25 wt.%, preferably between 2 and 12.5 wt.%, based on the combination of binding and solid material.
5. Use according to any one of claims 1-4, wherein the solid material comprises at least 70 wt.% biomass-derived material and/or at least 50% of wood, herbaceous plants or combinations thereof, and in particular comprises a material obtained by thermal treatment of semi-solid material, in particular by torrefaction, pyrolysis, gasification or partial combustion, more particularly torrefaction.
6. A process for producing a wear- and water-resistant solid fuel, comprising combining a solid carbonaceous material with between 1 and 25 wt.%, based on the combined weight, of a biomass torrefaction condensate (BTC) obtained by torrefying biomass at a temperature of between 240 and 350°C and condensing the volatized fraction of the torrefied biomass at a temperature which is between 100°C above and 50°C below the condensation temperature of water.
7. A process according to claim 6, wherein the BTC is added to said carbonaceous material and the material is subsequently densified.
8. A process according to claim 6, wherein the solid carbonaceous material is densified and the BTC is subsequently coated onto the solid material.
9. A process according to any one of claims 6-8, wherein the material is densified by being pelletised or briquetted.

10. A process according to any one of claims 6-9, wherein the organic material volatilised during torrefaction of biomass is directly condensed onto the solid carbonaceous material.
11. A process according to any one of claims 6-9, wherein the solid carbonaceous material comprises heat treated material, in particular heat-treated biomass.
12. A process for upgrading biomass comprising:
 - a. subjecting the biomass to torrefaction at a temperature of between 240 and 350°C, to produce a torrefied solid fraction and a volatilised fraction;
 - b. cooling the volatilised fraction to produce an organic condensate;
 - c. combining the condensate with a torrefied solid fraction;
 - d. densifying the torrefied solid fraction.
13. A process according to claim 12, wherein the torrefaction is performed at a temperature of between 240 and 320°C.
14. A process according to claim 12 or 13, wherein the weight ratio between said organic condensate and said torrefied solid fraction in step (c) is between 1:4 and 1:99.
15. A process according to any one of claims 12-14, wherein the condensate is combined with the torrefied solid fraction in the presence of water in an amount of 0.25-2.5 times the amount of condensate, and optionally other additives selected from organic solvents in an amount less than 1 time the amount of condensate.
16. A process according to any one of claims 12-15, wherein torrefied solid fraction is further pelletised and/or briquetted.
17. A torrefied biomass-derived material, suitable as a fuel, obtainable by the process according to any one of the preceding claims.
18. A torrefied material according to the preceding claim having one or more, preferably all, of the following characteristics:
 - a. a smallest outer particle size of between 2 mm and 10 cm;
 - b. a bulk density of between 0.35 and 1.0 kg/dm³, preferably between 0.65 and 0.9 kg/dm³;
 - c. a specific density between 0.8 and 1.5 kg/dm³, preferably between 1.1 and 1.4 kg/dm³;
 - d. a calorific value (Higher Heating Value (HHV)) of between 18 and 28 MJ/kg;

- e. a moisture content of less than 5 wt.%, also after storage at ambient conditions for at least 1 month;
 - f. a biomass-derived carbon content of at least 75%, i.e. a ^{14}C content of at least $5 \cdot 10^{-13}$ (0.5 ppt);
 - g. a grindability corresponding to a power consumption below 0.5 MJ/ton on a 0.25 mm mesh;
 - h. stability to ambient (outdoor) conditions for at least 1 month.
19. A torrefied material according to one of the preceding product claims, which comprises at least 95 wt%, preferably at least 99 wt.% material that originates from the biomass torrefaction process.
20. A torrefied material according to one of the preceding product claims, which comprises not more than 5 wt% other additives, which do not originate from the biomass torrefaction process.
21. Use of a BTC as an additive such as bio-bitumen, binding agent, filler or adhesive, lubricant, in a solid, preferably shaped material.

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2012/050541

A. CLASSIFICATION OF SUBJECT MATTER INV. C10L9/08 C10L5/36 C10L5/32 C10L5/14 C10L9/10 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C10L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EP0-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/129988 A1 (ANTHROTERRA PTY LTD [AU]; JOSEPH STEPHEN DAVID [AU]; FOIDL NIKOLAUS [A] 18 November 2010 (2010-11-18) page 10, line 18 - page 11, line 4 page 28, lines 1-28; figure 3 page 26, line 29 - page 27, line 4 -----	1-21
X	US 2010/251616 A1 (PAOLUCCIO JOHN A [US] ET AL) 7 October 2010 (2010-10-07) paragraphs [0051], [0052], [0069], [0130], [0194] figure 7 -----	1-21
X	US 2009/151251 A1 (MANZER LEO E [US] ET AL) 18 June 2009 (2009-06-18) paragraphs [0063] - [0064] ----- -/--	1-21
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 5 October 2012		Date of mailing of the international search report 19/10/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Bertin, Séverine

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2005 049375 A1 (KARLSRUHE FORSCHZENT [DE]) 26 April 2007 (2007-04-26) paragraph [0022] - paragraph [0023] -----	1-21
A	EP 2 236 587 A1 (GEN ELECTRIC [US]) 6 October 2010 (2010-10-06) paragraph [0038] paragraph [0044] - paragraph [0045] -----	1-21

INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2012/050541

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010129988 A1	18-11-2010	AU 2010246895 A1 CA 2761816 A1 CN 102459509 A EP 2430118 A1 US 2012125064 A1 WO 2010129988 A1	19-01-2012 18-11-2010 16-05-2012 21-03-2012 24-05-2012 18-11-2010
US 2010251616 A1	07-10-2010	NONE	
US 2009151251 A1	18-06-2009	CA 2707770 A1 CN 101896580 A EP 2231827 A2 US 2009151251 A1 US 2009151253 A1 WO 2009079127 A2	25-06-2009 24-11-2010 29-09-2010 18-06-2009 18-06-2009 25-06-2009
DE 102005049375 A1	26-04-2007	CA 2623148 A1 CN 101365770 A DE 102005049375 A1 EP 1934306 A1 US 2008236043 A1 WO 2007045291 A1	26-04-2007 11-02-2009 26-04-2007 25-06-2008 02-10-2008 26-04-2007
EP 2236587 A1	06-10-2010	CA 2697857 A1 EP 2236587 A1	02-10-2010 06-10-2010