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(54) PROCESS FOR CONVERTING BIOMASS TO COAL-LIKE MATERIAL USING HYDROTHERMAL CARBONISATION

(75) Inventor: **Markus Antonietti**, Bergholz-Rehbruecke (DE)

(73) Assignee: **CSL CARBON SOLUTIONS LTD.**, St. Helier, Jersey (JE)

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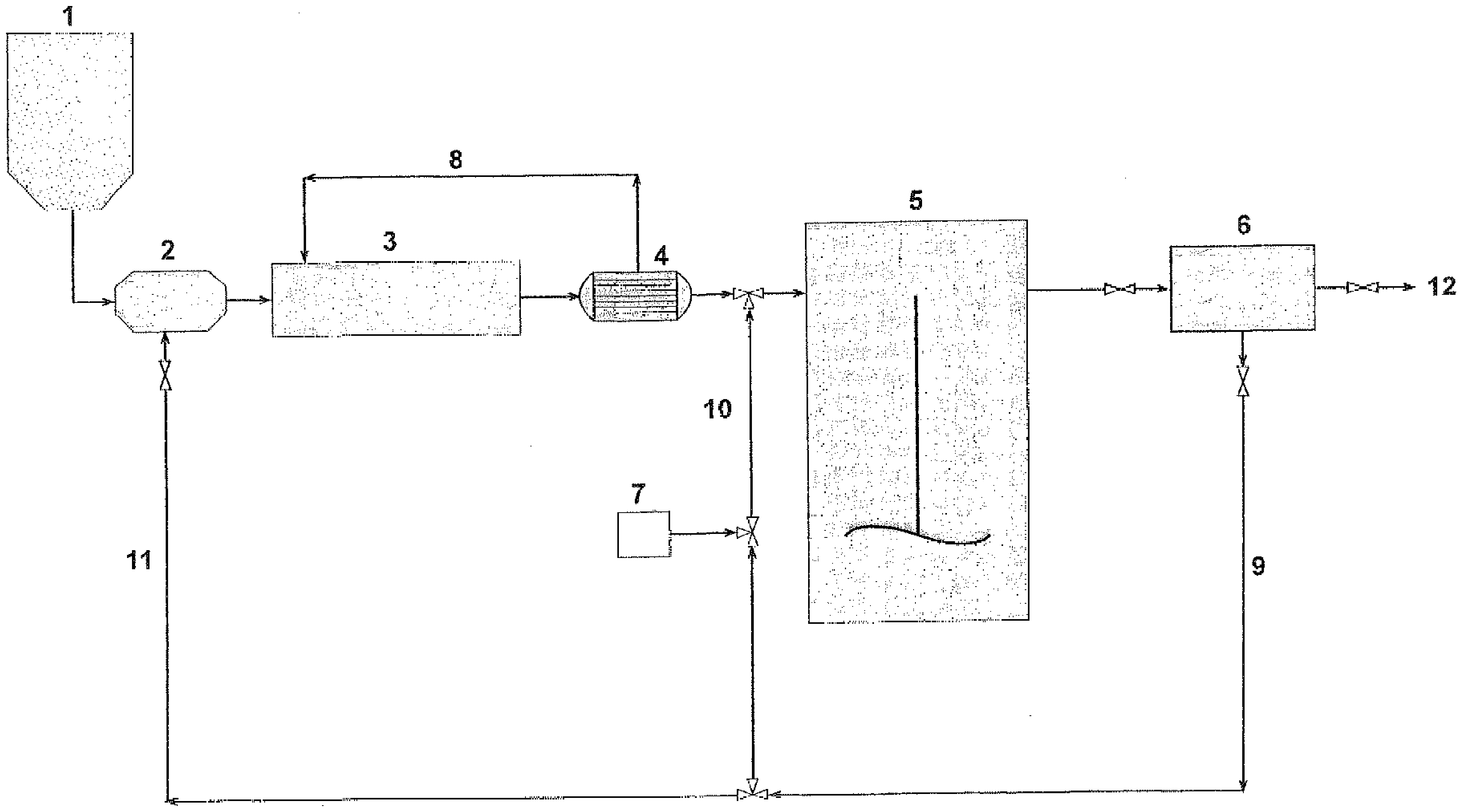
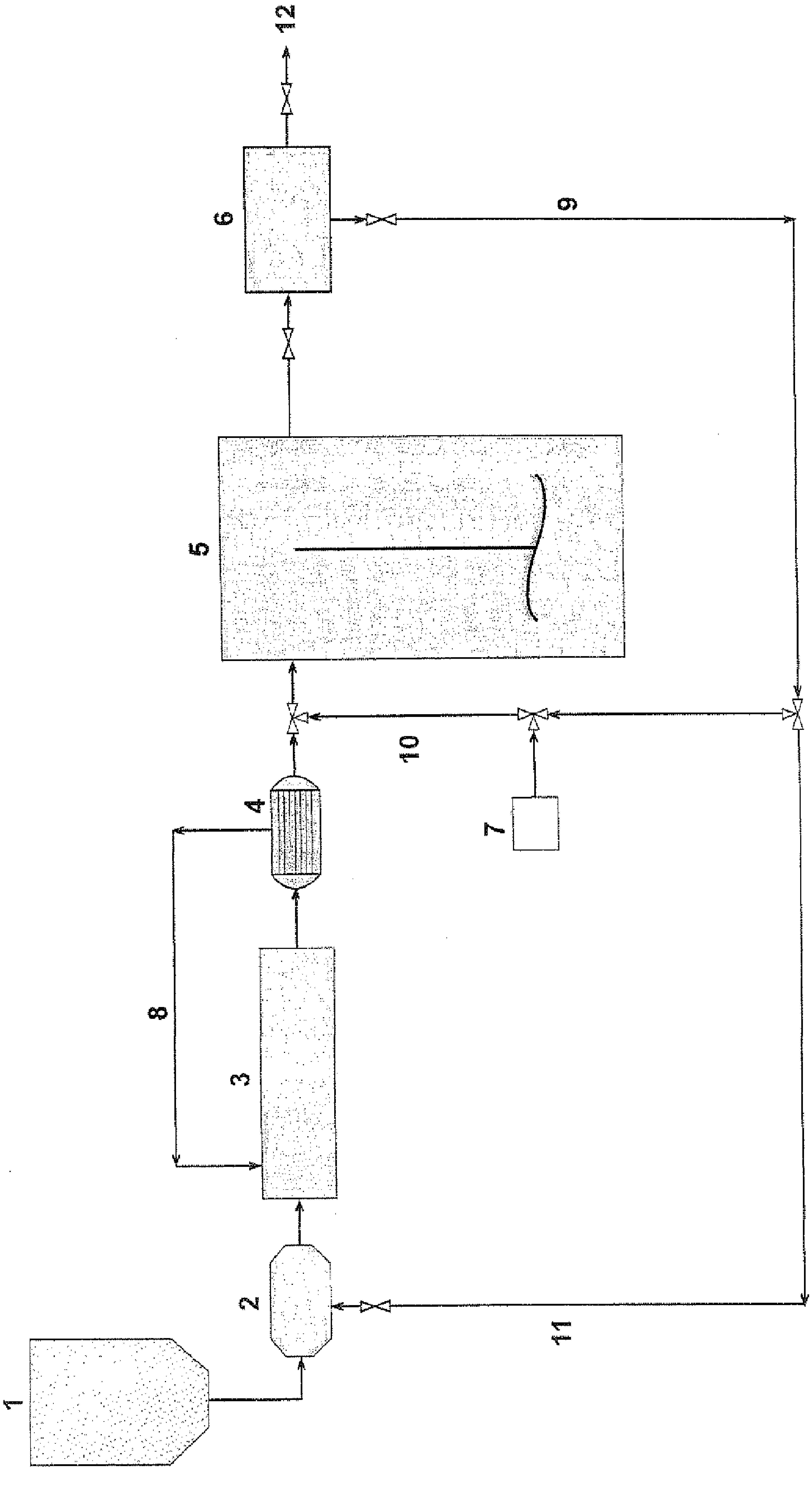
(57) ABSTRACT

The present invention relates to a hydro thermal carbonization process for the preparation of coal-like material using biomass. The process comprises a step (i) of heating a reaction mixture comprising water and biomass to obtain a reaction mixture comprising activated biomass; and a step (ii) of adding a polymerization initiator to the reaction mixture obtained in step (i) to polymerize the activated biomass and to obtain a reaction mixture comprising coal-like material. The process is beneficial in terms of product control, and process engineering.

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PROCESS FOR CONVERTING BIOMASS TO COAL-LIKE MATERIAL USING HYDROTHERMAL CARBONISATION

FIELD OF THE INVENTION

[0001] The present invention relates generally to a process for the preparation of coal-like material from biomass, more particularly to an improved and quicker process yielding the coal-like material in enhanced space-time yield, and which, moreover, allows for enhanced quality control of the final product, as well as improved reproducibility. Also, the process of the invention is cheaper in terms of the necessary equipment, and it is a very safe process.

BACKGROUND

[0002] In the past, many efforts have been made to imitate the natural coalification of biomass, which takes place on a time scale of some hundred (peat) to hundred million (black coal) years. Besides the formation of charcoal by pyrolysis of dry biomass, the so-called hydrothermal carbonization (HTC) process for the manufacture of coal or coal-like materials has recently attracted increasing attention. The first experiments were carried out already in 1913 by Bergius, who described the hydrothermal transformation of cellulose into coal-like materials. More systematic investigations were later performed by E. Berl et al. (Ann. Chem. 493 (1932), pp. 97-123; Angew. Chemie 45 (1932), pp. 517-529) and by J. P. Schumacher et al. (Fuel, 39 (1960), pp. 223-234). Recently, the hydrothermal carbonization has seen a renaissance starting with reports on the low temperature hydrothermal synthesis of carbon spheres using sugar or glucose as precursors (Q. Wang et al., Carbon 39 (2001), pp. 2211-2214 and X. Sun and Y. Li, Angew. Chem. Int. Ed. 43 (2004), pp. 597-601). Furthermore, metal/carbon hybrid nanostructures, such as nanocables prepared by a hydrothermal carbonization co-reduction process using starch and noble metal salts such as $AgNO_3$ as starting materials were described by S. H. Yu in Adv. Mater 16 (2004), pp. 1636-1640. H. S. Qian et al., in Chem. Mater 18 (2006), pp. 2102-2108 reported the synthesis of Te@carbon-rich composite nanocables and carbonaceous nanofibers by the hydrothermal carbonization of glucose.

[0003] M. M. Titirici et al., in. New J. Chem., 31 (2007), pp. 787-789 described the catalyzed HTC as an attractive alternative for the sequestration of carbon from biomass to treat the CO_2 problem. According to the paper, the optimum reaction conditions involve a heating of a biomass dispersion under weakly acidic conditions in a closed reaction vessel for 4-24 h to temperatures of around 200° C.

[0004] Generally, the HTC of biomass to afford carbon-like products was carried out as a one-step process.

[0005] US 2008/0006518 A1 relates to a process for reforming a biomass by heating the biomass in pressurized hot water to carbonize the biomass. According to a specific embodiment, the process comprises performing a primary heating of the biomass gradually at a temperature ranging from 200 to 260° C., and then performing a secondary heating of the biomass at a temperature ranging from 270 to 330° C. The products of the process are referred to as carbides. As mentioned in the document, the obtained carbides contain approximately 75 wt % of carbon. Owing to the temperatures close to the critical range which are used in the U.S. patent application, the process is complex and requires elaborate and thus expensive equipment to be carried out with safety.

[0006] The known processes for the preparation of coal-like materials left still room for optimization in terms of yield, efficiency and quality control of the final coal-like material. Accordingly, it is an object of the present invention to provide a process for the preparation of coal-like material from biomass which is quicker, more efficient and gives a higher yield of product, and which moreover allows an enhanced control and reproducibility of the quality of the final product in comparison to the methods of the prior art. A still further object resides in a process which requires less elaborate and expensive equipment and can nevertheless be carried out with high safety.

SUMMARY OF THE INVENTION

[0007] It has been surprisingly found by the present inventor that the above objects can be attained by a process for the preparation of coal-like material from biomass as recited in claim **1**, which is a process comprising a first activation step, and a second polymerization step, with the second step being initiated by the addition of a polymerization initiator to the reaction mixture obtained in the first, i.e. the activation step.

[0008] Preferred embodiments are subject of the dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The appended FIG. **1** provides a schematic flow diagram showing a preferred mode of carrying out the process of the invention in a continuous mode.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The process for the preparation of coal-like material according to the present invention can be referred to as a hydrothermal process, in particular as a hydrothermal carbonisation process. This terminology is intended to show that the process involves the heating of a reaction mixture comprising water and will yield carbonized coal-like material.

[0011] The term "biomass" as used herein is broadly understood as encompassing all kinds of plant and animal material and material derived from the same. According to a preferred embodiment, biomass as meant in the present specification shall not include petroleum or petroleum derived products.

[0012] The biomass for use in the present invention may comprise macromolecular compounds, examples of which are lignin and polysaccharides, such as starch, cellulose, and glycogen. As used herein, the term "cellulose" is intended to encompass hemicelluloses commonly also referred to as polyoses.

[0013] As will be appreciated, certain kinds of biomass may include both, plant and animal-derived material. As examples, manure (dung), night soil and sewage sludge can be mentioned. While the biomass for use in the present invention is preferably plant biomass, i.e. biomass of or derived from plants, certain contents of animal biomass (i.e. biomass of or derived from animals) may be present therein. For instance, the biomass may contain up to 30% of animal biomass.

[0014] According to a preferred embodiment, the biomass for use in the present invention, which is preferably plant biomass, contains more than 70 wt %, most preferably >90 wt %, of polysaccharides and lignines in terms of the solid contents of the biomass.

[0015] For instance, the plant biomass may be agricultural plant material (e.g. agricultural wastes) or all kinds of wood material.

[0016] Without limitation, examples of biomass are crop, agricultural food and waste, feed crop residues, wood (such as wood flour, wood waste, scrap wood, sawdust, chips and discards), straw (including rice straw), grass, leaves, chaff, and bagasse. Furthermore, industrial and municipal wastes, including waste paper can be exemplified.

[0017] The term "biomass" as used herein preferably also includes monosaccharides such as glucose, ribose, xylose, arabinose, mannose, galactose, fructose, sorbose, fucose and rhamnose, as well as oligosaccharides.

[0018] As is known to one of average skill in the art, "coal-like material", as used herein, refers to a material, which is similar to natural coal in terms of property and texture. Owing to the method of the preparation thereof, it may also be referred to as hydrothermal coal. It is a product, more precisely a carbonized product that is obtained or obtainable by the hydrothermal carbonization process of the invention.

[0019] As such, the coal-like material can be distinguished from synthetic resins, including those synthetic resins, which have been prepared using monomers obtained from lignocellulosic material, such as phenolic resins, and in particular novolac-type phenolic resins. Such synthetic resins are preferably not encompassed by the expression "coal-like material" as used herein.

[0020] The coal-like material obtained in the process of the present invention typically comprises, without limitation, <70 wt % of carbon, for example 60 to 65 wt % of carbon. Also, the coal-like material obtained in the process of the invention can have a carbon content of >50 wt % of carbon, which is significantly above the carbon content of dried (raw) biomass, which is in the order of 40 wt %. For instance, the coal-like material of the invention may comprise 65 to 72 wt % of carbon. As will be appreciated, the above carbon contents refer to the dry mass of the coal-like materials. In the present invention, the carbon content of the coal-like materials can be determined by elemental analysis (combustion). For instance, the carbon content of the materials can be measured using a Vario Micro analyzer (Elementar Analysensysteme, Hanau, Germany).

[0021] Moreover, as can be ascertained by way of solid state ^{13}C-NMR spectroscopy, the coal-like material as meant herein is more aliphatic than e.g. the product presumably obtained in US 2008/0006518, which is more aromatic.

[0022] The coal-like material obtained in the hydrothermal carbonisation process of the present invention has a high calorific value, for instance >23 MJ/kg, preferably 24 to 38 MJ/kg, and more preferably 24 to 32 MJ/kg. The calorific value of the coal-like material can be determined by standard calorimetry. More specifically, in the present invention, the calorific values of the materials can be determined in accordance with DIN 51900 or BGS RAL-GZ 724. As will be appreciated, the above calorific values of the coal-like material are expressed in terms of the dry mass of the coal-like material (in kg).

[0023] Both, the carbon content and the calorific value of the coal-like material are indicative of the high degree of carbonization of the coal-like material of the invention that can be achieved in the process of the present invention. According to a preferred embodiment, the coal-like material of the invention that is obtained by polymerization of the activated biomass initiated by the addition of a polymerization initiator in step (ii), has a carbon content of >50 wt % (in terms of the dry mass of the coal-like material) and a calorific value of >23 MJ/kg (in terms of the dry mass of the coal-like material). As meant herein, the "dry mass" of the coal-like material refers to the mass thereof after drying under such drying conditions that no further loss of water is observed. For instance, the dry mass can refer to the mass of the coal-like material after drying at a temperature of 80° C. for at least 24 h.

[0024] In the step (i), i.e. the first step, the biomass is activated for the subsequent polymerization to coal-like material in the second step.

[0025] Without wishing to be bound to theory, the mechanism of the activation in step (i) is assumed to be as follows. Upon heating, the macromolecular species, e.g. the polysaccharides contained in or constituting the biomass may be molten or dissolved in water. For instance, cellulose contained in the biomass, which is a crystalline material, will be molten in water. Moreover, the polysaccharides can be disintegrated or broken down to smaller fragments, such as monosaccharides and oligosaccharides. Those fragments will undergo consecutive rapid dehydration to more reactive intermediates, which are capable of undergoing rapid conversion to coal-like material, i.e. coalification, in the second step. Due to this capability, the reactive intermediates can also be referred to as "coal monomers". The dehydration of glucose to hydroxymethylfurfural is an example for such a dehydration reaction. These "coal monomers" are typically characterized by increased chemical reactivity towards intermolecular reactions, as compared to the raw biomass, e.g. via vinylic subunits, reactive aldehyde side groups, or activated hydroxymethyl groups onto furane moieties. For this reason, the first step of the hydrothermal carbonization process of the invention can also be referred to as the activation step, and the intermediate product of that step as activated biomass.

[0026] The water being present in the reaction mixture of the first step may be water adhering or bound to the original biomass, which can also be referred to as "raw" biomass. In this specification, the biomass to be subjected to step (i) is also referred to as raw biomass. As meant herein, raw biomass may for instance be the biomass obtained as waste (e.g. wood, agricultural, municipal waste) from the provider, without further treatment, or as collected from natural sources. In the case of wood, the raw wood biomass may be the wood collected in the forest (as the natural source), or sawdust from the wood processing industry. The water content of raw biomass may for instance be up to 80 wt %. As will be appreciated from the above, the raw biomass can be used as such and with water contents as mentioned above. Though drying is not excluded, e.g. in order to reduce the weight and consequently the transportation costs, the (raw) biomass to be subjected to the process of the invention is preferably not dried. Consequently, the present invention allows avoiding the energy-consuming drying of the biomass.

[0027] The presence of water in the process of the invention distinguishes this from e.g. pyrolytic processes for the conversion of biomass to coal-like materials by simple heating, typically in the absence of oxygen (carbonization).

[0028] In addition to the water present in, e.g. bound to the raw biomass such as obtained from natural sources, water may be added to the wet or dry biomass to adjust the water content in the reaction mixture of step (i). The total amount of water, i.e. the water bound to or contained in the as-obtained biomass and the additional water is not specifically limited.

Preferably, the weight ratio of water to biomass (water/biomass) in the reaction mixture of the first step is in the range of 0.3 to 10. For the ease of transportability, especially in a continuous process, the solid contents of the reaction mixture to be subjected to the step (i) is preferably 5 to 35%, more preferably 10 to 30%, especially 15 to 25% by weight. The reaction mixture having such solid contents is preferably in the form of a slurry.

[0029] The reaction mixture comprising water and biomass to be subjected to heating in the first step may comprise, without limitation, further ingredients as long as these will not inhibit the activation of the biomass.

[0030] The hydrothermal carbonisation process of the present invention can be carried out in water alone. Organic solvents such as ketones are unnecessary, and they are preferably omitted. According to a preferred embodiment, the reaction mixture of step (i) contains water as a single solvent, with other solvents such as ethanol only incidentially brought in by the biomass, e.g. by fermentation. Consequently, preferably at least 95 wt %, more preferably at least 98 wt % of the solvent present in the reaction mixture of the first step is water.

[0031] The present inventor found that an acidic pH in step (i) is advantageous. The pH is preferably in the range of 3 to 7, more preferably 4 to 6. By adjusting the pH to the acidic range, the disintegration, in particular of polymeric compounds in the biomass, e.g. by hydrolysis can be accelerated, and the yield of activated biomass, e.g. smaller fragments can be increased. There are kinds of biomass, which are more difficult to activate than others. Wood is an example of biomass, which is quite difficult to activate. In the case of biomass, which is more difficult to activate, the pH is adjusted to lie within the acidic range with particular benefit.

[0032] The desired pH of the reaction mixture in the first step can be controlled to lie within the above ranges by adding suitable acids, which do not interfere with the activation of the biomass. The acid is preferably a strong acid, e.g. having a pK_a of less than 4.5. Both, anorganic acids, e.g. mineral acids, and organic acids can be used. An example of a suitable mineral acid is phosphoric acid. Citric acid, lactic acid and pyruvic acid are examples of (strong) organic acids. According to a preferred embodiment, an acid such as those exemplified above is added to the reaction mixture prior to or during step (i) for the adjustment of the pH of the reaction mixture to lie in the range of 3 to 7, especially 4 to 6.

[0033] The reaction mixture to be subjected to the step (i), which may e.g. comprise an acid in addition to the (raw) biomass and water, can be prepared in a suitable mixer.

[0034] Dependent on which type of biomass is used as a starting material, the particular reaction conditions in step (i) may be selected appropriately. In particular, for biomass which can be activated relatively easily in step (i), such as monosaccharides, the duration of the activation step may be shorter and the pH less acidic than for polymeric biomass starting material.

[0035] The heating temperature (or the reaction temperature) in step (i) is not particularly limited, as long as it is sufficient to convert at least larger parts of the (raw) biomass subjected to the process to activated biomass as defined herein. Preferably, the heating temperature is such that at least 80 wt % of the raw biomass are converted to activated biomass. The heating temperature (or the reaction temperature) may be in the range of 190 to 270° C., and it preferably is 210 to 250° C., more preferably 230 to 240° C.

[0036] In this specification, the reaction temperature in step (i) is occasionally denoted T_1.

[0037] According to a particularly preferred embodiment, the temperature is 210 to 250° C., and the pH value is acidic, especially 3 to 7.

[0038] In the process of the invention, in particular under the above preferred reaction conditions in terms of temperature and pH, the reaction time of step (i) (i.e. until at least 80 wt % of the biomass have been converted to activated biomass as meant herein) can be reduced to 5 to 15 minutes, preferably 5 to 10 minutes. As will be appreciated, the duration of the first step will depend on the kind of biomass used.

[0039] The (raw) biomass to be subjected to the first step may be used in any form. Preferably, however it is divided into an appropriate particle size prior to use, e.g. in the range of 0.1 to 20 mm, more preferably 0.3 to 10 mm, especially 0.5 to 5 mm. Suitable particle sizes such as those exemplified above can be obtained by methods such as grinding, chopping or sawing.

[0040] The activated biomass present in the reaction mixture obtained in step (i) comprises the products of the disintegration and/or dehydration of the starting "raw" biomass as detailed above, collectively referred to as "activated biomass" in the present specification.

[0041] In step (ii), the activated biomass is subjected to polymerization to give coal-like material as defined above. To account for the fact that the "activated biomass" obtained in step (i) will be polymerized in step (ii), the "activated biomass" may in the alternative be referred to as "polymerizable biomass".

[0042] The polymerization in the second step is initiated by addition a polymerization initiator to the reaction mixture. The "polymerization" which takes place in the second step (i.e. in step (ii)) is to be construed broadly and means any reaction of molecules of the activated biomass resulting in the built-up of larger molecules eventually yielding coal-like material. The polymerization may include chain-growth of the monomers and inter-chain crosslinking. In the process of the invention, the polymerization will yield coal-like material, which preferably has, in terms of the dry mass thereof, a carbon content of >50 wt % and a calorific value of >23 MJ/kg. In the present invention, the polymerization initiator is added in step (ii) as a reactant to initiate the polymerization resulting in coal-like material, which preferably has a carbon content and calorific value as indicated above.

[0043] According to a particularly preferred embodiment, the reaction mixture obtained in step (i) is directly subjected to step (ii), i.e. without any intermediate treatment. However, the reaction mixture obtained in step (i) may be cooled by allowing to stand or by active cooling, prior to adding the polymerization initiator to start step (ii).

[0044] It may be noted that some polymerization of components contained in the activated biomass may take place already in step (i). The polymerization step (ii) as such is initiated by adding the polymerization initiator.

[0045] The polymerization initiator for use in the present invention is not specifically limited in kind, as long as it is suitable to initiate the polymerization of the activated biomass to the carbon-like material in the second step of the hydrothermal carbonization process of the present invention. At the reaction conditions of the second step, the polymerization initiator is usually capable of generating radicals which will start the polymerization of the activated biomass to coal-like material.

[0046] Useful polymerization initiators are for instance azo compounds, peroxides, oxygen and redox initiators, as well as mixtures thereof. The azo compound may be azobisisobutyronitrile. Useful peroxides are inorganic peroxides, e.g. persulfates such as potassium persulfate and ammonium persulfate; metal peroxides such as $(C_2H_5)_2BOOC_2H_5$ and compounds obtained by replacing the boron atom of $(C_2H_5)_2BOOC_2H_5$ with Al or Zn; organic peroxides, e.g., acyl peroxides such as benzoyl peroxide, alkyl peroxides such as t-butyl peroxide and cumyl peroxide, peroxy acid esters such as t-butyl peroxalate, or hydrogen peroxide. As the redox initiator, there may be used hydrogen peroxide-Fe^{2+} (Fenton's reagent), persulfate and sulfite and cumene hydroperoxide-amine-based compounds. In addition, copper salts such as $CuCl_2$ can be used. In the alternative and most preferably, $FeCl_3$ and H_2O_2 are used as the redox initiator.

[0047] More specifically, polymerization initiators known to be useful for the hardening of unsaturated polyesters are also useful to initiate the polymerization in the second step of the present process.

[0048] One specific type of polymerization initiators useful in the present invention is commonly referred to as warm hardeners. Warm hardeners are typically peroxides which will be decomposed at their decomposition temperature to form a radical which will start the polymerization, i.e. carbonization, to yield the target coal-like material. Examples of such peroxides are benzoyl peroxide, cumolhydroperoxide, methylisobutylketonperoxide, and tert.-butylperoxybenzoate. As will be appreciated, the reaction mixture in the second step is preferably heated to or above the decomposition temperature of the peroxide to generate radicals, when warm hardeners are used as polymerization initiators.

[0049] The second type of polymerization initiators which are likewise useful in the process of the present invention are often referred to as cold hardeners, e.g. in the field of unsaturated polyesters. Cold hardeners representing suitable polymerization initiators for use in the present invention generally comprise an accelerator compound and a peroxide, the peroxide being added with preference after the accelerator compound. Examples of the accelerator compound are iron salts. Suitable peroxides are e.g. acetylacetone peroxide, methylethylketone peroxide and cyclohexanone peroxide. Further examples of the cold hardeners are amine-based accelerators, such as dimethyl aniline and diethylenaminetetracetate, in combination with benzoyl peroxide. As suggested by the name, cold hardeners do not require any heating to form radicals to start the polymerization in the second step.

[0050] In order to avoid any contamination of the product, i.e. the coal-like material obtained in step (ii), the polymerization initiator does preferably not contain any metal. If the initiator contains any metal, the metal content in the coal-like material is adjusted to preferably not more than 0.5 wt %, more preferably not more than 0.1 wt %.

[0051] Due to the addition of the polymerization initiator, the reaction temperature can be kept much lower in the second step of the process of the invention in comparison to the prior art such as US 2008/0006518 A1. In particular, the reaction temperature in the second step can be lower than in the first step. This allows for carrying out the process in less elaborate equipment, e.g. in a simple autoclave and has also significant benefits in terms of the reproducibility of the process and the quality control of the end product. Furthermore, in comparison to the one-step processes of the prior art, the polymerization, i.e. carbonization to the coal-like material will proceed much quicker, e.g. by a factor of 3 to 10.

[0052] For instance, the reaction temperature in the second step (occasionally denoted T_2 in this specification) can be in the range of 140 to 220° C., preferably it is 170 to 210° C., and more preferably 180 to 200° C. According to a particularly preferred embodiment, the temperature in the second step is below the temperature in the first step. For instance, the reaction mixture may be heated to a temperature in the range of 210 to 250° C. in the first step, and to a temperature in the range of 170 to below (i.e. not including) 210° C., especially to 180 to 200° C. in the second step. This is a particularly preferred embodiment. According to another preferred embodiment, the reaction temperature in the first step may be 220 to 250° C., and in the second step to 170 to 210° C.

[0053] Without limitation, the polymerization in the second step may be finished for instance within 1 to 3 hours. That is, within that time frame, a coal-like material of reproducible quality can be obtained. Of course, the reaction can be carried out longer or shorter if desired.

[0054] The process according to the present invention is preferably carried out in a pressure resistant reactor, e.g. an autoclave or an extruder. Due to the water in the reaction mixture, there will be a pressure increase upon heating. As the hydrothermal carbonization reaction is exothermic, external heating may no longer be necessary, once the reaction, e.g. in the first step, has started, provided the thermal insulation of the reactor or reactors is sufficient.

[0055] For the purpose of this specification, the reaction temperature is meant to refer to the temperature, more specifically the average temperature, inside the reaction mixture, which can be measured with a thermocouple. Consequently, it is readily possible to control the reaction temperature to lie within the desired range by heating or cooling the reactor, as appropriate.

[0056] Subsequent to the second step, the solid phase comprised or consisting of the coal-like material can be separated from the reaction mixture, e.g. by filtration or decantation, preferably by filtration, while a liquid phase will remain. Without restriction, this separation, in particular the filtration can take place at the elevated temperatures of the second reactor, thus allowing an advantageous heat management of the reaction system. Then, the coal-like material can be dried.

[0057] As the present inventor found out, the residual liquid phase obtained in the separation subsequent to step (ii) can be reused in the hydrothermal carbonisation process of the invention with particular benefit. For instance, the above liquid phase, which preferably contains >80 wt %, more preferably >90 wt % of water can be oxidized to obtain an oxidized liquid phase. This can be done with any oxidizing agent, as long as this has a suitable oxidation potential to effect the oxidations as outlined hereinafter, and as long as the oxidizing agent or the reaction products thereof does not interfere with the further uses of the (oxidized) liquid phase as detailed below. Examples of useful oxidizing agents are, without limitation, oxygen, hydrogen peroxide, percarbonate, and percarbonic acids. Preferably, the oxidizing agent is an oxygen-containing gas, which is preferably air. In the case of the oxygen-containing gas, such as air, the oxidation of the liquid phase can be effected by bubbling the gas through the liquid phase, stirring the liquid phase in an atmosphere of the gas or by allowing the liquid phase to stand in the presence of the gas.

[0058] According to an alternative embodiment, the reaction mixture obtained in the second step which contains the liquid (aqueous) phase, rather than the (separated) liquid phase as such is oxidized, and the oxidized liquid phase is subsequently separated from the solid phase of the coal-like material in the reaction mixture.

[0059] The present inventor has discovered that the liquid phase in the mixture obtained in the second step, as a result of the hydrothermal carbonization process, contains e.g. ethers and ketones (such as laevulic acid), which can be converted into the corresponding peroxides through the oxidation. Examples of the peroxides are ketone peroxides, such as hydroxyacetone peroxides. These (hydro)peroxides can be recycled to the second step of the reaction, and be used as a polymerization initiator.

[0060] Moreover, it was found out by the present inventor that strong organic acids such as lactic acid or pyruvic acid will be generated during the hydrothermal carbonization process of the present invention. Hence the liquid phase obtained in the second step can also be recycled to the first step, where these acids will be effective in accelerating the activation, in particular the disintegration as detailed above. If desired, the liquid phase obtained in the second step can be subjected to oxidation, as explained above, prior to recycling to the first step.

[0061] As meant herein, the recycling of the liquid phase to the first step also covers the embodiment where it is recycled to the mixing unit (to be further explained hereinafter) from which it will be transferred to the reactor in which the step (i) is to be carried out.

[0062] With an eye on the heat management, the optionally oxidized liquid phase preferably is still hot (e.g. it has a temperature of e.g. 50-220° C., preferably 90-220° C., most preferably 140-180° C.) when it is introduced in the reaction mixture of the first step and/or the second step.

[0063] Using the separated liquid (aqueous) phase from the second step (with or without oxidation) to admix it to the biomass prior to or during the first step of the hydrothermal carbonization process of the invention has a number of benefits. For instance, the water content (and hence also the viscosity) of the reaction mixture in the first step can be optimally adjusted. Moreover, the heat included in the separated liquid phase can be reused in the process.

[0064] According to a preferred embodiment, the liquid phase of the reaction mixture in the second step is divided into two parts, one of which is recycled (with or without oxidation) to the first step for pH management, and the second of which is recycled (after oxidation) to the second step to make up for consumed polymerization initiator. As will be appreciated, the liquid phase from the second step may be subjected to the oxidation prior to dividing this into the above two parts. In addition, the caloric heat can be handled efficiently, when the respective parts of the liquid phase are recycled when still hot. As will be appreciated, the above recycling is particularly advantageous in a continuous flow system. Generally speaking, the above recycling allows for a minimization of side products and an optimization of the carbon yield in the hydrothermal carbonization process of the invention.

[0065] Using the aqueous liquid phase of the second step for process reasons (both, as a carrier of heat and of chemically active components) is also beneficial from the point of view of sustainability. Side products in the water phase (i.e. the aqueous liquid phase) only cumulate up to their solubility limit while afterwards the equilibrium reactions under HTC conditions (in particular in the second step) ensure that the yield of coal-like material is increased. For these reasons, bringing the reaction water (i.e. the aqueous liquid phase) into the reaction multiple times has a beneficial influence on both the reaction kinetics as well as the carbonization yield, i.e. the yield of the coal-like material.

[0066] In relation to the one-step hydrothermal carbonization processes of the prior art, the two-step process of the present invention, in which the first step is preferably characterized by higher temperature, shorter residence time, higher reaction viscosity (due to the raw biomass), and higher technical demands, and in which the second step is preferably characterized by comparably longer residence time, lower temperatures and pressures, and a more passive reaction handling also exhibits many processing advantages.

[0067] Specifically, the reactor, in which the first step is to take place, which step, due to the preferably higher temperature and pressure, is more demanding from a process engineering point of view than the second, can be kept rather small, which is safer and moreover gives better heat transfer.

[0068] For instance, the reactor for carrying out the first step can be an extruder. Extruders allow very high pressures of up to 700 bars, temperatures of up to 400° C., are made for viscous starting materials, are regarded as very reliable and safe. Moreover, extruders allow effective and rapid heating and the injection of additional reactants at desired positions.

[0069] In a most preferable version, the temperature of the reaction mixture containing the activated biomass is reduced downstream, e.g. at the end of the extruder to the desired reaction temperature of the second step, making use of an efficient heat exchanger, and the heat is used for the preheating of the biomass to be subjected to the first step.

[0070] As lower temperature and pressure can be employed in the second step due to the addition of the polymerization initiator, less demanding and safer constructions of the reactor(s) to be used in the second step are possible in the hydrothermal carbonization process of the invention. As heat is produced throughout the hydrothermal carbonization process (it is a highly exothermic process) the reactor(s) for use in the second step—sufficient insulation provided—may not require further external heating and may be heated by recirculation of the cooling liquid of the first step.

[0071] Without restriction of generality, the second reaction step can be carried out in a cascade of smaller reactors, which improves the residence time within the second step and gives an improved coal-like material.

[0072] By reference to the appended FIG. **1**, a preferred mode of carrying out the process for the preparation of coal-like material according to the present invention will be illustrated. As can be seen, the process schematically shown in the flow diagram provided in the figure is a continuous process.

[0073] Reference numeral **1** denotes a (raw) biomass storage vessel. Preferably, the biomass contained in the vessel **1** has a suitable particle size, e.g. in the range of 0.1 to 20 mm. From the storage vessel **1**, the biomass is fed to a mixing unit **2** where it is mixed with further ingredients such as water and acid to give a reaction mixture. A stream **11** of the (aqueous) liquid phase separated in the separating unit **6** is recycled to the mixing unit **2** to provide at least part of the water and acid. According to a preferred embodiment, the stream of the aqueous liquid **11** (comprising acids) is mixed with the biomass in the mixing unit **2** without adding any further ingredients. Moreover, the separated liquid phase **11** preferably has a temperature of 140 to 220° C. The reaction mixture obtained in the mixing unit **2** is then transferred to the reactor **3** in which the step (i) is carried out. The reactor **3** is preferably an extruder as detailed above. The reaction temperature T_1 may be between 190 and 270° C. The reaction mixture comprising activated biomass obtained in the reactor **3** is then transported through a heat exchanger **4**, from which the heat energy **8** can be recycled to the reactor **3**. The reaction mixture comprising activated biomass leaving the heat exchanger **4** is transferred to the reactor **5** for carrying out the polymerization step (ii). The reactor **5** is a pressure vessel, e.g. an autoclave. Preferably, it is provided with stirring means, which are schematically shown in the figure. The internal temperature in the reactor **5** may be between 140 and 220° C. To the reactor **5**, a polymerization initiator may be added from the external (not shown). In the alternative or in addition, oxidized aqueous liquid phase **10** separated in the separating unit **6** and containing suitable peroxides is fed along with the reaction mixture comprising activating biomass to the reactor **5**. The reaction mixture comprising coal-like material obtained in the step (ii) is transferred from the reactor **5** to the separating unit (e.g. filtration unit) **6**, in which it is separated into a solid phase of the coal-like material **12**, and an (aqueous) liquid phase **9**. In the continuous process illustrated in the figure, the liquid phase **9** is split into two parts. The first part is recycled as stream **11** (preferably having a temperature between 140 and 220° C.) to the mixing unit **2**. The second part is oxidized by adding a suitable oxidizing agent from the oxidizing unit **7** to obtain species in the oxidized liquid phase **10** which can act as a polymerization initiator and can as such be recycled to the reactor **5** as detailed above.

[0074] While the above description was focussed on the hydrothermal carbonization process, the present invention, according to a preferred embodiment, relates to the coal-like material obtained or obtainable by the process of the invention as such which is preferably characterized by the physical characteristics, in particular the carbon content and the calorific value as detailed above.

[0075] The present invention will be further understood from the following examples, which are given by way of illustration and must not be construed in a limiting sense. In the examples, the carbon content of the materials was determined with a Vario Micro analyzer (Elementar Analysensysteme, Hanau, Germany), and the calorific value of the materials was measured in accordance with BGS RAL-GZ 724.

EXAMPLES

Example 1

[0076] 6.0 g glucose is dissolved in 24.0 g water, and citric acid is added to adjust the pH to 5. A 40 ml stainless steel autoclave is charged with the mixture and heated to 230° C. for 5 min. After cooling, the autoclave is opened, and 30 mg benzoyl peroxide is added under stirring. Then, the autoclave is sealed again, and heated to 180° C. After 90 min, the reaction is terminated by quenching. 2.9 g of hydrothermal coal containing 64 wt % carbon is obtained. The calorific value of the coal is 26 kJ/g.

Example 2

[0077] 200 g wood flour (sawdust) and 600 g water are formed into a slurry, and phosphoric acid is added to adjust the pH to 4. A 1 l stainless steel autoclave (manufactured by Paar, Germany), equipped with an internal thermoelement, is charged with the mixture and heated to 250° C. After exceeding the internal temperature of 240° C., the reaction is quenched after 10 min. Subsequently, 100 mg $FeCl_3.6\ H_2O$ and 200 mg 30% aqueous H_2O_2 are added at a temperature of about 100° C. The reaction mixture is heated again to 195° C., and further reacted for 3 h. After cooling and opening the autoclave, the product is separated into a solid phase (containing the hydrothermal coal) and a liquid phase. There is obtained 76 g of hydrothermal coal which contains 68 wt % carbon and can be pulverized by hand. The calorific value of the coal is 25 kJ/g.

Example 3

[0078] The liquid phase separated from the reaction mixture in Example 2, while still warm (60° C.), is bubbled with air to obtain an oxidized liquid phase. Then, Example 2 is repeated except for using 200 ml of the thus-obtained oxidized liquid phase in place of the $FeCl_3.6\ H_2O$ and H_2O_2. A product is obtained which is, within the measurement accuracy, the same as that obtained in Example 2.

1. A hydrothermal carbonization process for the preparation of coal-like material from biomass, characterized by comprising at least the following steps:

heating a reaction mixture comprising water and biomass to obtain a reaction mixture comprising activated biomass; and

(ii) adding a polymerization initiator to the reaction mixture obtained in step (i) to polymerize the activated biomass and to obtain a reaction mixture comprising coal-like material.

2. The process of claim **1**, wherein the polymerization initiator is selected from oxygen, peroxides, azo compounds and redox initiators.

3. The process of claim **1**, wherein the amount of the polymerization initiator is 0.01 to 2 wt %, in terms of the reaction mixture.

4. The process of claim **1**, wherein the reaction mixture is heated to a temperature in the range of 210 to 250° C. during step (i).

5. The process of claim **1**, wherein the reaction mixture has a pH in the range of 3 to 7, preferably 5 to 7, in step (i).

6. The process of claim **1**, wherein an acid is further added to the reaction mixture prior to or during step (i).

7. The process according to claim **1**, wherein step (ii) is carried out at a temperature in the range of 140 to 220° C.

8. The process according to claim **7**, wherein the temperature in step (i) is above the temperature in step (ii).

9. The process according to claim **1**, wherein the coal-like material is the product of the polymerization in step (ii).

10. The process according to claim **1**, wherein the coal-like material has, in terms of the dry mass thereof, at least one of the following features (a) and/or (b):

(a) a carbon content of >50 wt %;

(b) a calorific value of >23 MJ/kg, preferably >24 MJ/kg.

11. The process according to claim **1**, further comprising the step of separating the reaction mixture obtained in step (ii) into a solid phase of the coal-like material, and a liquid phase.

12. The process according to claim **11**, wherein the liquid phase obtained in the separation step is oxidized to obtain an oxidized liquid phase.

13. The process according to claim **12**, wherein the oxidation is carried out by contacting the liquid phase with an oxygen-containing gas.

14. The process of claim **13**, wherein the oxygen-containing gas is air.

15. The process according to claim **12**, wherein the, optionally oxidized, liquid phase is recycled to step (i) and/or (ii).

16. A coal-like material obtainable by a hydrothermal carbonization process according to claim **1**.

17. The coal-like material of claim **16**, which has in terms of the dry mass thereof, a carbon contact of >50 wt % and a calorific value of >23 MJ/kg.

18. The process of claim **3**, wherein the amount of polymerization initiator is 0.05 to 0.2 wt %, in terms of the reaction mixture.

19. The process of claim **5**, wherein the reaction mixture has a pH in the range of 5 to 7, in step (i).

20. The process according to claim **7**, wherein step (ii) is carried out at a temperature in the range of 170 to 210° C.

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