

(19)



(11)

EP 4 574 930 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.06.2025 Bulletin 2025/26

(21) Application number: **23315464.0**

(22) Date of filing: **20.12.2023**

(51) International Patent Classification (IPC):
C10G 1/08 (2006.01) **C10G 21/04** (2006.01)
C10G 21/08 (2006.01) **C10G 21/28** (2006.01)
C10G 1/06 (2006.01)

(52) Cooperative Patent Classification (CPC):
C10G 1/065; C10G 1/083; C10G 21/04;
C10G 21/08; C10G 21/28; C10G 2300/1011;
C10G 2300/1014; C10G 2300/1018

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR
 Designated Extension States:
BA
 Designated Validation States:
KH MA MD TN

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(54) **PROCESS FOR TREATING A CARBONACEOUS LIQUID FEEDSTOCK FROM A HYDROTHERMAL LIQUEFACTION TREATMENT**

(57) The invention relates to a hydrothermal liquefaction of an initial carbonaceous feedstock (1) in order to obtain a biocrude:

- step a) mixing the feedstock (1) with a catalyst and a liquid,
- step b) hydrothermal liquefaction (5) of the mixture (3),
- step c) liquid/liquid/gas separation (8) of the liquefaction product (7) in order to obtain a first gaseous phase (31), a second liquid aqueous phase (10) and a second liquid organic phase (18) known as biocrude,
- step d) of separation of the second aqueous phase (10) in order to obtain a third liquid aqueous phase (12), and a first phase of water vapor (22),
- step e) of dilution of the second liquid organic phase (18)
- step f) of contacting the dilute biocrude (20) with at least one solvent (17,23,24), with liquid-liquid counter-stream extraction, so as to obtain, on the one hand, a raffinate (25) and on the other hand an extract (16),
- step g) of separation of the raffinate (25) so as to obtain the mineral-depleted biocrude (27) and a phase (9,28) comprising the diluent,
- step h) of condensation of the first vapor phase (22) and recycling as a solvent (17) in step (f),
- a step i) recycling of the extract (16) to step (d),
- a step (j) of separation of a second part of the first vapor phase (22).

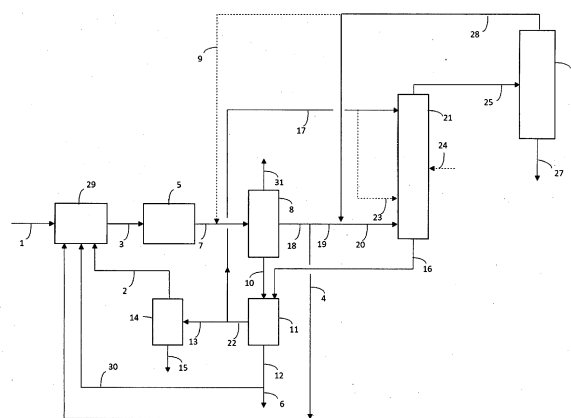


FIG.1

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Description

Technical Field

[0001] The present invention relates to the production of recoverable chemicals or biofuels from biomass, including lignocellulosic biomass. More specifically, the invention relates to biomass hydrothermal liquefaction processes, also known by the acronym HTL for "Hydro-Thermal Liquefaction", which make it possible to transform biomass into a carbon feedstock called "biocrude". This so-called "biocrude" must then be treated, including notably hydroconversion, hydrotreatment, hydrocracking, catalytic cracking, to obtain the desired chemicals to the desired specifications.

Technical background

[0002] Hydrothermal liquefaction (see "Continuous Hydrothermal Liquefaction of biomass: a critical review", D. Castello, T. H. Pederson, L. A. Rosendahl, *Energies* 2018, 11, 3165) is a process of converting a charge in the presence of water at a pressure between 100 and 350 bar (between 10^7 Pa and $3.5 \cdot 10^7$ Pa) and at a temperature between 250 and 450°C . Catalysts can be used for hydrothermal liquefaction, like pH modifiers, NaOH, KOH, K_2CO_3 , Na_2CO_3 , etc. The products of hydrothermal liquefaction are called "biocrude", consisting mainly of organic molecules, an aqueous phase comprising water-soluble organic compounds (alcohols, acids, ketones, phenols, etc.) and salts, gases and possibly biochar. Biochar is a carbon-rich solid product, "char" deriving from the English word "charcoal". The gas produced consists mainly of CO_2 but can also contain hydrogen, methane, and CO.

[0003] In the hydrothermal liquefaction process, water may be present in liquid form or in a relatively dense supercritical state. Water close to the critical point (374°C , 221 bar) has very different properties than those of water at room temperature. These near-critical properties allow water to play several roles in the conversion process such as being a reactant, a catalyst, or a source of hydrogen. Near the critical point or in the supercritical state, water has properties that facilitate liquefaction such as a low dielectric constant that allows solubilization of nonpolar molecules and an ionic product high enough to favor ionic reactions leading to liquid products over free radical reactions leading to solid or gaseous products.

[0004] The reactions taking place in the hydrothermal liquefaction process are numerous and complex, but one can mention depolymerization reactions including hydrolysis, dehydration, decarboxylation, and repolymerization reactions including condensation.

[0005] The yield and composition of the biocrude depend on the operating conditions, but also on the feedstock treated with hydrothermal liquefaction. For example, for a feedstock made of wood, hydrothermal liquefaction obtains a mass yield of around 40-45% of bio-

crude and of gas of 40-45% as well.

[0006] The hydrothermal liquefaction feedstock can be biomass, preferably selected from plants, grasses, trees, wood chips, seeds, fibers, seed husks, aquatic plants, algae, hay, and other sources of lignocellulosic materials, such as those from organic waste, municipal waste, agri-food waste, animal waste, forestry waste, sawmill waste, logging residues, agricultural and industrial waste (such as sugarcane bagasse, oil palm waste, sawdust, or straw). The feedstock of hydrothermal liquefaction can also come from paper pulp and paper by-products, recycled or not, or from by-products from paper mills, waste such as used plastics, worn tires. The filler can also be a mixture of two or more of these materials.

[0007] Biocrude obtained by hydrothermal liquefaction is a complex mixture of compounds, consisting mainly of hydrocarbons and oxygenated compounds. In general, oxygenated compounds are organic acids, ketones, oxygenated aromatic compounds, alcohols, aldehydes, esters, ethers, and water. Water usually accounts for less than 15% by weight of the biocrude. In the case of a lignocellulosic biomass load, the biocrude contains compounds from cellulose, hemicellulose, and lignin (the structure found in lignocellulosic biomass).

[0008] The biocrude obtained by hydrothermal liquefaction has an oxygen, sulfur and nitrogen content that varies greatly depending on the feedstock of the hydrothermal liquefaction (algae, wood, etc.). For example, the biocrude from hydrothermal liquefaction of wood is generally made up of 5 to 20% weight of oxygen, less than 0.5% weight of sulfur and less than 5% weight of nitrogen in the dry biocrude (without water).

[0009] Biocrude can contain up to 4% weight of inorganics (mineral compounds), mainly metals such as sodium, potassium but also calcium, iron, etc. These mineral compounds can come from the catalysts used for hydrothermal liquefaction, from the hydrothermal liquefaction feedstock itself, and from the metals possibly used to grind the hydrothermal liquefaction feedstock. Sodium and potassium can be present in relatively large quantities in the biocrude, as the hydrothermal liquefaction process typically uses alkali-based catalysts (NaOH, KOH, K_2CO_3 , Na_2CO_3 ...) in significant quantities.

[0010] This content of inorganics, especially metals, generally does not allow the biocrude to be used as a fuel because the amount of ash is too high.

[0011] To be transformed into biofuels (petrol, kerosene, diesel, marine fuel oil) or chemicals, biocrude must be processed, in particular with a view to reducing heteroatoms and more particularly the oxygen it contains. This treatment may include at least one operation chosen from hydroconversion, hydrotreatment, hydrocracking, or catalytic cracking. However, these operations use catalysts known to the skilled person as sensitive to metal content (in particular to alkali or alkaline earth metals such as Na, K, Ca, etc.). These metals poison the catalysts: they deactivate them at least partially.

[0012] It is therefore necessary to purify the biocrude,

i.e., to reduce its content of mineral compounds, especially metallics, so that its subsequent treatments can be carried out.

[0013] It is known from patent applications WO18177877, WO19092173, WO21121662 treatments aimed at purifying biocrudes, and in particular to recover the metal salts they contain for recycling, with different types of separation devices, using acidic aqueous phases or washing agents, but the implementation of these separation/treatment operations seems complex.

[0014] The aim of the invention is to develop a hydrothermal liquefaction process integrating a treatment of the product obtained, such as biocrude, to reduce the content of mineral compounds, in particular metals, a process that is preferably simple to implement, and preferably economical in terms of tools and/or consumption of utilities.

Summary of the invention

[0015] The invention relates first of all to a hydrothermal liquefaction of an initial carbonaceous feedstock at least partly derived from biomass, in order to obtain a so-called biocrude product with a reduced content of mineral compounds, said process comprising the following steps:

- step a) mixing the initial carbonaceous feedstock with at least one catalyst and at least one liquid phase, including at least a first aqueous phase containing all or part of the catalyst and optionally at least a first organic phase,
- step b) of hydrothermal liquefaction of the mixture obtained in step a), in order to obtain a liquefaction product,
- step c) of liquid/ liquid/gas separation of the liquefaction product obtained in step (b), in order to obtain a first gaseous phase, a second liquid aqueous phase and a second liquid organic phase known as a biocrude, (part of which is optionally recycled as an organic phase in stage (a) of mixing)
- step (d) of separation by heating of the second aqueous phase obtained in step (c), in order to obtain a third liquid aqueous phase enriched with minerals from at least the catalyst used in stage (a) of mixing, and a first phase of water vapor,
- step (e) of dilution of the second liquid organic phase, called biocrude, obtained in step (c) with a diluent comprising an organic liquid phase which has a lower viscosity and density than said second liquid organic phase known as biocrude, so as to obtain a dilute biocrude,
- a step (f) of contacting the dilute biocrude obtained in step (e) with at least a solvent comprising a liquid aqueous phase, with counter-stream liquid-liquid extraction, so as to obtain, on the one hand, a raffinate comprising the mineral-depleted biocrude and diluent, and on the other hand an extract comprising the mineral-enriched solvent,

- a step (g) of separation of the raffinate obtained in contact step (f) so as to obtain, on the one hand, the biocrude depleted in mineral compounds and, on the other hand, a phase comprising the diluent,
- a step (h) of condensation of a first part of the first vapor phase obtained in step (d) and recycling of said first part of the first vapor phase once condensed as a solvent for contacting step (f),
- a step (i) of at least partial recycling of the extract obtained in contacting step (f) to step (d) of separation by heating,
- a step (j) of separation of at least a second part of the first vapor phase obtained in step (d), in order to obtain a fourth aqueous phase, and a first so-called light organic phase (possibly recycled as an organic phase in mixing step (a)).

[0016] It should be noted that several of these steps can be performed in the same device or set of devices. Thus, mixing and liquefaction can be carried out in the same equipment or not.

[0017] It should also be noted that the recycling steps mentioned can be carried out in the form of recycling loop(s) of the considered fluid, that they can therefore be carried out continuously or discontinuously in the process, and that the statement of the steps does not mean that the steps are necessary successive and consecutive: the process may include other optional steps, in addition to the recycling steps that may take place throughout the process or during a certain period of the process.

[0018] It should be noted that, for all the recycling described in this text, the recycling may be only partial, i.e., the whole stream under consideration or only part of it can be recycled, and that, in addition, this recycling may be supplemented by an input from an external stream. (e.g., an external water supply when the flow to be recycled is of the aqueous type, or an input of external organic products when the flow to be recycled is of the organic type.

[0019] The aqueous phase is mainly defined as a phase, which is mainly aqueous, but which may contain soluble organic compounds and/or mineral compounds. In the same way, an organic phase is understood to be a phase that is mainly organic, but which may contain a (low) water content and/or other compounds, such as mineral compounds.

[0020] The invention, if it can be summarized synthetically, consists in integrating in a single process

- on the one hand a process for hydrothermal liquefaction of a feedstock comprising biomass, (with premixing, liquefaction and liquid/liquid/gas separation)
- and on the other hand the treatment of the biomass feedstock once liquefied to deplete it of mineral compounds (with dilution, liquid/liquid extraction and separation), so that it can then be converted

conventionally without mineral compounds interfering (too much) with subsequent conversion reactions. This allows to maintain the type of catalyst usually used for these conversion steps, such as hydroconversion, hydrotreating, hydrocracking, or catalytic cracking.

[0021] And this integration is a high level integration, with very relevant recycling operations that make it possible to reduce or even eliminate the consumption of certain utilities of the process as a whole, and one can, according to the invention, implement both internal recycling during the liquefaction, internal recycling in the mineral depletion treatment of the liquefied biomass, and recycling between the liquefaction and the depletion treatment.

[0022] Thus, recycling according to step i) of the extract obtained at the contacting step towards the separation step d) is very advantageous: this extract, as detailed below, is an aqueous solution rich in mineral compounds, and recycling it in the separation step d) will allow these mineral compounds to be recycled, ultimately, towards step b) of liquefaction: These mineral compounds include metal compounds from catalysts used in liquefaction. This recycling therefore makes it possible to reduce or even eliminate the consumption of catalysts in the hydrothermal liquefaction stage of the biomass.

[0023] And step (h) of condensing the first part of the first vapor phase obtained in step (d) and recycling the first part of the first vapor phase once condensed as a solvent in step (f) is also very advantageous, as it also helps to reduce the water consumption of the process as a whole.

[0024] In addition, the treatment of the biocrude, resulting from the separation step c) after liquefaction b) in order to reduce its mineral compound content, is also in itself very efficient: And to do this, the treatment first uses dilution with a "light" organic diluent (less dense and less viscous than biocrude), then a liquid/liquid extraction counter-stream wide, with an aqueous solvent. And it turned out that this combination of dilution + extraction is very effective.

[0025] Counter-stream liquid/liquid extraction can be implemented quite simply, by an extraction column such as gravity extraction column for example (or several columns in series or parallel).

[0026] Extracting in such a column requires a sufficient difference in density between the phases present (often greater than 50 kg/m³), and the greater the difference in density, the easier it will be. In addition, the viscosity of one or both phases plays an important role in this operation, as the more it increases, the more the transfer of material between phases will be slowed down on the one hand, and the more the capacity of the column is likely to decrease, in terms of the possible feedstock rate per column section unit on the other hand. Counter-stream columns are interesting because they allow the desired solutes to be extracted much better than in a co-stream

column or in a stirred tank. Indeed, the number of theoretical stages can reach high values (between 2 and 15 in the vast majority of cases), and with minimized solvent consumption.

[0027] Advantageously, the first so-called light organic phase obtained in step (j) can be at least partly recycled as the first organic phase in mixing stage (a).

[0028] Advantageously, at least part of the second liquid organic phase known as the biocrude obtained in step (c) of liquid/liquid/gas separation may be recycled as the first organic phase in mixing stage (a).

[0029] Advantageously, the method according to the invention may comprise a step (k) of at least partial recycling of the phase comprising the diluent obtained in step (g) of separation as a diluent in step (e) of dilution. This recycling can be partial or total: it can be supplemented by an addition of external diluent, if necessary, but it is very interesting, because it makes it possible to drastically reduce the consumption by diluting the treatment process according to the invention.

[0030] Advantageously, the method according to the invention may comprise a step (l) of at least partial recycling of the phase comprising the diluent obtained in step (g) of separation in step (c) of liquid/liquid/gas separation. This recycling of the diluent phase, which is in fact a light fraction of biocrude, at the c) liquid/liquid/gas separation has been shown to improve the liquid/liquid/gas separation.

[0031] Advantageously, the method according to the invention may comprise a step (m) of at least partial recycling of the third liquid aqueous phase in mixing step (a). This phase is aqueous and may contain mineral compounds, its recycling in mixing step a) reduces both the water and catalyst consumption of the hydrothermal liquefaction.

[0032] Advantageously, the method according to the invention may comprise at least a recycling step of the first organic phase and/or the second organic phase in the mixing step (a) (via flow 4 as detailed below). This additional recycling option reduces the consumption in the organic phase required for the pre-liquefaction mixing operation.

[0033] Preferably, step b) of hydrothermal liquefaction involves heating, at a temperature between 250°C and 450°C under a pressure between 100 bar (10⁷ Pa) and 350 bar (3.5.10⁷ Pa), in the presence of at least one catalyst containing at least a pH modifier and/or an alkaline, such as Na or K, and/or an alkaline earth such as Ca.

[0034] Preferably, the diluent used in the dilution step (e) is selected from a light cut in the biocrude filler or a chemical compound or mixture of chemical compounds, including alcohols, ethers, ketones, and hydrocarbons. The process can be started with a diluent with a boiling temperature close to that of the phase comprising the diluent to be recycled according to step (g), which is a light cut of the biocrude, then this phase will gradually accumulate in the recycling loop over time and will thus gradually replace the initial diluent.

[0035] Preferably, in dilution step (e), the diluent has a final boiling point of at most 150°C, preferably at most 100°C.

[0036] Preferably, at the end of step (e) of dilution, the dilute biocrude has a dynamic viscosity at 20°C of at most 7 cP, preferably at most 4 cP, and a density at 15°C of at most 950 kg/m³, preferably at most 900 kg/m³.

[0037] Preferably, in dilution step (e), the ratio R of the flow rate Qd of the diluent to the flow rate Qb of the biocrude is at most 10, and in particular at least 0.1, with the ratio R preferably between 0.5 and 3.

[0038] Preferably, contact step (f) is carried out at a pressure between 0.5.10⁵ Pa and 15.1 Pa, and at a temperature between 15 and 150°C, while remaining below the boiling temperature of the diluent at the contact pressure.

[0039] Preferably, step (d) of separation and/or step (g) of separation and/or step (j) of separation is a treatment consisting of at least evaporation, distillation, heating followed by separation. Preferably, the diluent used in step (e) of dilution is selected from a light cut in the biocrude filler or a chemical compound or mixture of chemical compounds, including alcohols, ethers, ketones, and hydrocarbons.

[0040] Preferably, the solvent used in contacting step (f) is selected from at least one of the following solutions: pure aqueous solution, demineralized aqueous solution, aqueous solution containing soluble organic compounds, acidic aqueous solution. In the case of an acidic aqueous solution, it may contain from 10 ppm to 20% weight of an organic or mineral acid, strong or weak, such as acetic acid, nitric acid, sulfuric acid, hydrochloric acid, citric acid, oxalic acid, lactic acid, formic acid, or any other acid.

[0041] One or at least one of the solvents, when there are several ones, may also be an aqueous solution acidified by injection of carbon dioxide into the aqueous solution (which may already contain one of the above-mentioned acids). Indeed, the hydrothermal liquefaction step prior to treatment according to the invention tends to generate carbon dioxide, which can therefore be advantageously used to acidify the solvent(s), if necessary.

[0042] Preferably, as seen above, all or part of this solvent used for contacting step (f) comes from the recycling of at least part of the first vapor phase from separation step (d), once condensed.

[0043] Only one type of solvent can be used, e.g., injected at the top, at the head of the column operating the liquid/liquid extraction (when it is vertically oriented), with a possible second injection point at an intermediate height. Depending on one variant, two separate solvents can be used, which are brought into contact with the diluted biocrude in separate contact zones, e.g., with the first injected at the top/head of the column and the second at an intermediate column height.

[0044] These two options can also be combined, preferably with the second injection point of the first solvent at a column height lower than the injection point of the

second solvent:

- For example, at least one of the inlets of the second solvent is at an intermediate height of the column, in particular at a height H₂ in relation to the total height H of the column such that the ratio H₂/H is between 0.2 and 0.8.
- it is also possible that it is rather one of the inlets of the first solvent which is at an intermediate height of the column, in particular at the height H₂ in question.

[0045] The total height H is the useful height of the column, which is known in the field of liquid-liquid extraction or distillation columns. If the first solvent (or the second solvent) has a second inlet in the column at an intermediate height H₃, then this intermediate height H₃ is preferably lower than the height H₂ of the inlet of the second solvent (or first solvent). Advantageously, this height H₃ of the second inlet of the first solvent (or of the second solvent) can be such that, H being the total height of the column, the ratio H₃/H is between 0.05 and 0.4.

[0046] The solvent is preferably aqueous. When there are preferably two solvents the first is at a neutral pH (between 6.5 and 7.5, possibly containing soluble organic molecules) while the second is acidic (pH less than 6.5, with the addition of acid (e.g. an acidic aqueous solution containing from 10 ppm to 20% weight of at least one strong or weak acid, organic or mineral, in particular selected from at least one of the following acids: acetic acid, nitric acid, sulfuric acid, hydrochloric acid, citric acid, oxalic acid, lactic acid, formic acid, and possibly soluble organic molecules).

[0047] Preferably, contacting step (f) includes a dedicated or additional settling (decantation) to improve the settling between the two aqueous and organic phases. The settling device used (e.g., a decanter) may be located after/downstream of the column or after/downstream of the last liquid-liquid extraction column (when there are several ones) or between two liquid-liquid extraction columns in series that are used in separation step (c). The extraction column (or one of those used in step c) may have a short-residence time settling function, which tends to separate the phases in a non-optimal manner, and it is possible that a fraction of residual free water (droplets) may be entrained in the raffinate. In this case, a decanter can be placed downstream (line 25 detailed below) to better separate the water (and not upstream of the column). If the contact between the two liquid phases is made via two separate columns, then a decanter can be placed between the two columns, or only one at the outlet of the second column (or no decanter at all).

[0048] Preferably, step (f) of contacting the dilute biocrude (20) obtained in step (e) is carried out with at least two separate solvents, which are brought into contact with said dilute biocrude in separate contact zones and comprising a first solvent which is an aqueous liquid phase with a neutral pH, in particular between 6.5 and 7.5, and a second solvent which is an acidic aqueous

liquid phase, having a pH of less than 6.5.

[0049] The invention also relates to a hydrothermal liquefaction facility of a feedstock derived at least in part from biomass, with a view to obtaining a so-called biocrude product, with a reduced content in mineral compounds, in particular metallics, which implements the process described above.

[0050] The invention also relates to a facility of hydrothermal liquefaction of an initial carbonaceous feedstock at least partly derived from biomass, in order to obtain a so-called biocrude product with a reduced content of mineral compounds, the said facility comprising the following devices :

- a device (a) for mixing the initial carbonaceous feedstock with at least one catalyst and at least one liquid phase, including at least one first aqueous phase containing all or part of the catalyst and optionally at least one first organic phase,
- a device (b) for hydrothermal liquefaction of the mixture obtained with the mixing device (a) in order to obtain a liquefaction product,
- a device (c) for the liquid/liquid/gas separation of the liquefaction product obtained in step (b), in order to obtain a first gaseous phase, a second liquid aqueous phase and a second liquid organic phase, called biocrude (part of which is optionally recycled as an organic phase in the mixing device (a))
- a device (d) for heating the second liquid aqueous phase obtained with the liquid/liquid/gas separation device (c), in order to obtain a third liquid aqueous phase enriched with minerals from at least the catalyst used in the mixing device (a) and a first water vapor phase ,
- a device (e) for diluting the second liquid organic phase called biocrude obtained with the device (c) for liquid / liquid/gas separation with a diluent comprising an organic liquid phase which has a lower viscosity and density than those of second liquid organic phase called biocrude, so as to obtain a dilute biocrude,
- a device (f) for contacting the dilute biocrude obtained with device (e) for dilution with at least one solvent comprising a liquid aqueous phase, said device comprising a counter-stream liquid-liquid extraction column, preferably gravity-based, so as to obtain, on the one hand, a raffinate comprising the biocrude depleted in mineral compounds and diluent, and, on the other hand, an extract comprising the solvent enriched in mineral compounds,
- a device (g) for separating the raffinate obtained with the device (f) for contacting, so as to obtain, on the one hand, the biocrude depleted in mineral compounds and, on the other hand, a phase comprising the diluent,
- a device (h) for condensing part of the first vapor phase obtained in step (d) and for recycling said part of the first vapor phase once condensed as a solvent

in contacting step (f),

- a device (i) for recycling at least part of the extract obtained with the contacting device (f) towards the device (d) for separating by heating
- a device (j) for separating at least a first part of the first vapor phase obtained with the device (d), in order to obtain a fourth aqueous phase, and a first so-called light organic phase, possibly recycled as an organic phase in the mixing device (a).

[0051] The devices implementing the steps of the process described above are included. As already stated, some of the devices may be common to multiple steps/operations.

[0052] The (e) dilution device may be a tank-type device fed by both the biocrude feedstock and the diluent. It can also be achieved simply by a plurality of inlet pipes that converge to a common pipe(s) where mixing/dilution is carried out dynamically towards the contacting device, using appropriate valves.

[0053] The contacting device (f) is preferably a liquid/liquid extraction column with gravitational counter-stream. It can be a single column or a plurality of columns, mounted in series or in parallel. The column(s) are generally equipped at the top and /or bottom of the column with settling devices (decantation devices), and additional settlers can be added at the top (light phase) outlet of each column, their role having been detailed above.

[0054] The facility according to the invention may also comprise a recycling device of at least part of the phase comprising the diluent obtained with device (g) as a diluent for the dilution device (e). This recycling device can be made up of pipe(s) providing a fluidic connection between the two devices g) and f) and controlled in a known way by valves.

[0055] The facility according to the invention may provide that the contacting device (f) comprises a counter-stream liquid/liquid extraction column equipped at the bottom of the column and/or at the head of the column with a settling device f1), f2).

[0056] The facility according to the invention may also comprise a device (k) for recycling at least part of the phase comprising the diluent obtained with the separation device (g) as a diluent in dilution step (e).

[0057] The facility according to the invention may also comprise a device (l) for at least partial recycling of the phase comprising the diluent obtained with the separation device (g) into the liquid/liquid/gas separation device (c).

[0058] The facility according to the invention may also comprise a device (m) for at least partial recycling of the liquid aqueous third phase to the mixing device (a).

[0059] The facility according to the invention may also comprise a device for at least partial recycling of the first organic phase and/or the second organic phase (notably via the flow 4 detailed below) to the mixing device (a).

[0060] The or at least each of the recycling devices is preferably in the form of pipes or sets of pipes ensuring

the appropriate fluidic connection to form recycling loops that can be controlled, in particular by means of valve systems (at least some of these recycles may also provide for intermediate storage of the streams to be recycled in tanks).

[0061] Preferably, the separation device (d) by heating the liquid aqueous second phase and/or the separation device (g) and/or the separation device (j) comprises at least one device chosen from a distillation column, an evaporator, an exchanger followed by a separator flask, in particular a so-called "flash" separator flask.

[0062] Preferably, the facility comprises a recycling device for at least part of the phase comprising the diluent obtained with the separation device (g) as a diluent for the dilution device (e).

[0063] Preferably, the contacting device (f) comprises a counter-stream liquid/liquid extraction column, preferably gravity-based, and preferably equipped at the bottom of the column and/or at the head of the column with a settling device (f1) and/or (f2).

[0064] The invention also relates to a biomass treatment process comprising hydrothermal liquefaction of biomass, then treatment to reduce the mineral content of the biocrude obtained, as described above, and then a conversion treatment of the treated biocrude such as hydroconversion, hydrotreating, hydrocracking, catalytic cracking in order to produce biofuels and/or other chemical compounds (called bio-based compounds).

List of Figures

[0065] Figure 1: This figure shows in a very schematic way a facility implementing the biocrude treatment process according to the invention.

[0066] This figure therefore does not represent all the equipment in the installation, but those that are most useful for understanding the invention. The different devices and others are not necessarily to scale, nor necessarily represented in space as they can be in an industrial facility.

[0067] The list of references is as follows:

- 1 - initial feedstock comprising biomass
- 2 - organic phase of light organic compounds from the fractionation (separation) device 14
- 3 - mixture from the mixing device 29
- 4 - phase obtained from the solid/liquid separation device 8 having treated the biocrude from the hydrothermal liquefaction device 5
- 5 - Hydrothermal Liquefaction Device
- 6 - Flow from separation device 11 and Intended for purge
- 7 - Liquefaction Product : Effluent from hydrothermal liquefaction device 5 and feeding Liquid /Liquid/Gas separation device 8 (water and biocrude Mixture)
- 8 - Liquid/Liquid/Gas Separation Device
- 9 - Stream fraction 28 which is a light fraction of the biocrude accumulated in a recycling loop

- 10 - Aqueous phase
- 11 - Separation device
- 12 - Liquid aqueous phase obtained from the separation device 11
- 13 - Vapor phase from of the vapor phase 22
- 14 - separation device
- 15 - aqueous phase from the separation device 14
- 16 - extract from the liquid-liquid extraction column 21
- 17 - liquid aqueous phase from the vapor phase 22 for injection as a solvent (or first solvent when there are several) at the head of the liquid/liquid extraction column 21
- 18 - organic phase from the liquid/liquid/gas separation device 8
- 19 - biocrude from liquid/liquid/gas separation device 8, corresponding to phase 18 from which a fraction 4 could be removed
- 20 - Mixing of Biocrude Stream 19 and Stream 28
- 21 - Liquid/Liquid Extraction Column
- 22 - Vapor Phase obtained from Separation Device 11
- 23 - Optional First Solvent injection Point in Liquid/Liquid Extraction Column 21
- 24 - Optional Injection Point for second optional solvent in the liquid/liquid extraction column 21
- 25 - Raffinate, i.e. organic effluent from the liquid/liquid extraction column 21
- 26 - Separation device
- 27 - "demineralized" biocrude, i.e., depleted of mineral compounds
- 28 - a light fraction of the biocrude accumulated in a recycling loop
- 29 - Mixing device
- 30 - aqueous phase containing one or more catalysts
- 31 - gaseous phase from the liquid/liquid/gas separation device 8

Description of embodiments

[0068] The invention aims to treat biomass-containing feedstocks by hydrothermal liquefaction, in order to obtain a liquefied biomass which is also depleted of mineral and metallic compounds.

[0069] As a reminder, the feedstock of hydrothermal liquefaction can be biomass, preferably chosen from plants, grasses, trees, wood chips, seeds, fibers, seed husks, aquatic plants, algae, hay and other sources of lignocellulosic materials, such as those from organic waste, municipal waste, agri-food waste, animal waste, forestry waste, sawmill waste, logging residues, agricultural and industrial waste (such as sugarcane bagasse, oil palm waste, sawdust or straw). The feedstock of hydrothermal liquefaction can also come from paper pulp and paper by-products, recycled or not, or from by-products from paper mills, waste such as used plastics, worn tires. The feedstock can also be a mixture of two or more of these materials.

[0070] For the purposes of the invention, the initial feedstock may be a type of biomass or a mixture of two or more of these types of biomass. It cannot be ruled out that the initial feedstock may also contain a share of hydrocarbon feedstock that is not of biomass origin, but in this case this share is preferably (very) minority.

[0071] As a reminder, the characteristics of a biocrude-type feedstock after hydrothermal liquefaction of interest to the invention may be the following: The biocrude obtained by hydrothermal liquefaction is a complex mixture of compounds consisting mainly of hydrocarbons and oxygenated compounds. In general, oxygenated compounds are organic acids, ketones, oxygenated aromatic compounds, alcohols, aldehydes, esters, ethers, and water. Water usually accounts for less than 15% by weight of the biocrude.

[0072] In the case of a lignocellulosic biomass load, the biocrude contains compounds from cellulose, hemicellulose, and lignin (structure present in lignocellulosic biomass).

[0073] The biocrude obtained by hydrothermal liquefaction has an oxygen, sulfur and nitrogen content that varies greatly depending on the load of the hydrothermal liquefaction (algae, wood, etc.). For example, the biocrude from hydrothermal liquefaction of wood is generally made up of 5 to 20% weight of oxygen, less than 0.5% weight of sulfur and less than 5% weight of nitrogen in the dry biocrude (without water).

[0074] Biocrude can contain up to 4% weight of inorganics, mainly metals such as sodium, potassium but also calcium, iron, etc. Inorganics can come from catalysts used for hydrothermal liquefaction, from the hydrothermal liquefaction charge, and from metals used to grind the hydrothermal liquefaction charge. Sodium and potassium can be present in significant quantities in the biocrude because the hydrothermal liquefaction process uses alkali-based catalysts (NaOH, KOH, K₂CO₃, Na₂CO₃, etc.) in significant quantities.

[0075] The biocrude is generally characterized by a kinematic viscosity at 50°C between 10 and 40,000 cSt, a dynamic viscosity at 50°C between 10 and 40,000 cP, a density at 15°C between 0.9 and 1.2 and a final distillation temperature exceeding 750°C.

[0076] Biocrude has a very wide distillation range, from room temperature to over 750°C. For example, for a biocrude from hydrothermal liquefaction of wood, about 10% weight of the biocrude is vaporized in the range 20-180°C, 10% weight to 45% weight of the biocrude is vaporized in the interval 180-350°C and 45% weight to 80% weight of the biocrude is vaporized above 350°C.

[0077] Figure 1 shows a facility for implementing the invention, which will be described below.

[0078] The feedstock to be liquefied supplies the process with stream 1. This feedstock 1 may be biomass preferably chosen from plants, grasses, trees, wood chips, seeds, fibers, seed husks, aquatic plants, algae, hay, and other sources of lignocellulosic materials, such as e.g., those from organic waste, municipal waste, agri-

food waste, etc. animal waste, forestry waste, sawmill waste, felling residues, agricultural and industrial waste (such as sugar cane bagasse, waste from oil palm cultivation, sawdust, or straw). The load of hydrothermal liquefaction can also come from paper pulp and paper by-products, recycled or not, or by-products from paper mills, waste such as used plastics, worn tires. Feedstock 1 can be a combination of the loads listed earlier.

[0079] This process feedstock 1 is mixed in mixer 29 with streams 2, 30 and 4:

- Stream 2 is made up of light organic compounds and is derived from fractionation 14 described below.
- Stream 30 contains catalysts and chemicals in water and is derived from fractionation 11 described below.
- Stream 4 is a fraction of the biocrude produced by hydrothermal liquefaction and comes from separator 8 described below.

[0080] Stream 3 from mixer 29 feeds into hydrothermal liquefaction section 5, where stream 3 is heated, pressurized, converted, and finally cooled to form stream 7.

[0081] Stream 7 feeds a gas-liquid-liquid separator 8.

[0082] The products coming out of separator 8 are a gas 31, an aqueous phase 10, an organic phase 18 called biocrude, part 4 of which is recycled to mixer 29, and the rest 19 is sent to the liquid-liquid extraction column 21.

[0083] An optional variant of the process (dotted line in the figure) is to mix stream 7 with stream 9 which is a fraction of stream 28, a light fraction of the biocrude accumulated in a recycling loop described below, in order to improve separation in separator 8.

[0084] The aqueous stream 10 undergoes a separation operation 11 by boiling temperature (flash, distillation, evaporation...) to concentrate the catalysts and chemicals in its liquid output 12, which is partly purged by stream 6 and partly recycled via stream 30 to the mixer 29.

[0085] The steam output 22 from separation 11 contains no minerals, and it is divided into 2 streams, stream 13 in vapor form and stream 17 in liquid form, obtained by condensation of a fraction of stream 22:

- Stream 13 is subject to a new separation step 14 by boiling temperature, with the objective of recovering organic compounds 2 in order to recycle them to mixer 29. The stream 15 obtained at the bottom of separation 14 contains mainly water.
- Stream 17, composed mainly of water and water-soluble organics, is used as a solvent to demineralize the biocrude in the liquid-liquid extraction column 21.

[0086] Biocrude 19 is mixed with stream 28 to form stream 20 called dilute biocrude.

[0087] Stream 28 is a light fraction of the biocrude, accumulated in a recycling loop described below. This mixture is made to reduce the density and viscosity of the

biocrude (dilution) and thus make it easier to process in the gravity liquid-liquid extraction column 21.

[0088] The dilute biocrude 20 feeds the liquid-liquid extraction column known as gravity column 21 at its bottom and has a mass flow rate Q_m . Column 21 extends along a vertical or essentially vertical longitudinal axis.

[0089] Liquid-liquid extraction is carried out using a solvent 17 consisting of an aqueous solution, resulting from the condensation of steam 22 which may be treated or supplemented with additives. It can be pure water, demineralized water, water with soluble organic molecules, an acidic aqueous solution containing from 10 ppm to 20% weight of an acid such as acetic acid, nitric acid, sulfuric acid, hydrochloric acid, citric acid, oxalic acid, lactic acid, formic acid or any other acid, or a mixture of these different aqueous solutions.

[0090] The liquid-liquid extraction column 21 is supplied at its bottom by stream 20.

[0091] The liquid-liquid extraction column 21 is fed at the head by stream 17 which is an aqueous solvent containing mainly water and water-soluble organic compounds.

[0092] An optional variant of the process is to inject another solvent of different composition, such as an acidic aqueous solvent 24, in an intermediate position on the height of column 21, in order to improve the extraction of inorganics.

[0093] Another optional variant, if an injection of aqueous solvent acid 24 is used, is to inject a part of the non-acid aqueous solvent 17 into the lower position of the column (stream 23). In this case, stream 23 is injected lower than stream 24 into the column.

[0094] Biocrude 19 from the hydrothermal liquefaction unit has a flow rate of Q_b . Biocrude 19 is mixed with recycled diluent 28 with a flow rate of Q_d such as $0.1 < Q_d/Q_b < 10$ and preferably $0.5 < Q_d/Q_b < 3$. Flow rates are measured in mass per unit of time.

[0095] Recycled diluent 28 is preferably a compound or mixture of compounds with a dynamic viscosity at 20°C less than 4 cP, and usually not less than 0.3 cP, and a density at 15°C between 600 and 850 kg/m³. Dilution is carried out by providing a pipe in the supply line from biocrude 19 to the extraction column 21: the mixture between the biocrude and the diluent is operated in the common pipe portion downstream of the tapping. ("upstream" and "downstream" are understood in this text by considering the progression of the biocrude feedstock in the facility).

[0096] Mixture 20, biocrude + diluent, called "dilute biocrude", has here a dynamic viscosity at 20°C less than or equal to 7 cP, preferably less than or equal to 4 cP and a density at 15°C less than or equal to 950 kg/m³, preferably less than or equal to 900 kg/m³, and generally not less than 600 kg/m³. These properties are obtained by choosing an appropriate diluent type and diluent flow rate (in relation to the biocrude flow rate).

[0097] Diluent 28 can be a light cut present in the biocrude (the process can start with an initial diluent,

which will gradually be replaced by the recycled phase containing the diluent, as indicated above) or a chemical compound (or a mixture of chemical compounds) present or not present in the biocrude. The diluent can consist of compounds from the family of alcohols, ethers, ketones, and hydrocarbons, for example.

[0098] The final boiling point of diluent 28 is preferably less than or equal to 150°C, and preferably less than or equal to 100°C. It is preferably at least 60°C.

[0099] Solvent 17 feeds top of column 21 (column head) with a flow rate Q_s . The Q_s flow rate of solvent 17 is chosen such as $0.05 < Q_s/Q_m < 5$ and preferably $0.3 < Q_s/Q_m < 3$.

[0100] Extraction column 21 has the following features:

- Operating pressure P between 0.5 bar abs ($0.5 \cdot 10^5$ Pa) and 15 bar abs ($1.5 \cdot 10^5$ Pa), preferably between 0.9 bar abs ($0.9 \cdot 10^5$ Pa) and 1.5 bar abs ($1.5 \cdot 10^5$ Pa).
- Operating temperature T between 15°C and 150°C, preferably between 20°C and 60°C
- T/S between 5 and 80 m/h, preferably between 10 and 40 m/h, with:

S is the cross-section of column 2, in m²

T is the total volume traffic in column 21, where T is defined as follows

$T = Q_m/\rho_{\text{hom}} + Q_s/\rho_{\text{os}}$, expressed in m³/h

[0101] With ρ_{hom} and ρ_{os} the densities, e.g., in kg/m³, of the dilute biocrude 20 and solvent 17 respectively under the operating conditions of column 21 (pressure, temperature).

[0102] The useful height of column 21 is between 1.5 m and 50 m high, preferably between 1.8 m and 25 m. The column can be of different types: packed column, perforated plate column, mechanical stirring column, pulsed column or other.

[0103] In column 21, two phases are mixed and brought into contact: an organic phase (dilute biocrude 20) and an aqueous phase (solvent 17). In column 21, one phase is dispersed into the other, which is the continuous phase.

[0104] The organic phase is called the light phase because its density is lower than the other phase, the aqueous phase. The aqueous phase is called the heavy phase.

[0105] The dispersed phase can be the heavy phase (solvent 17) or the light phase (dilute biocrude 20), but preferably the light phase (dilute biocrude 20). If the dispersed phase is the heavy phase (solvent 17), the column is preferably equipped with a decanter at its bottom. The decanter will be at the head of the column if the dispersed phase is the light phase (dilute biocrude 20). It is also possible to provide a decanter at the bottom and at the head of the column.

[0106] Column 21 makes it possible to reach a theoretical number of stages between 2 and 15, and preferably

between 2.5 and 7.

[0107] The effluents in column 21 are:

- A raffinate 25 consisting mainly of the biocrude, the diluent and the compounds present in the solvent (mainly water). The amount of inorganics/mineral compounds present in raffinate 25 is much lower than in dilute biocrude 20, due to the efficiency of liquid-liquid extraction. Organic effluent 25 in column 21, referred to as raffinate, contains dilute biocrude that is demineralized, i.e., has a reduced inorganic content. This stream 25 feeds a separation operation 26 to separate the demineralized biocrude 27 from a light cut 28, which is recycled to dilute the biocrude before entering the liquid-liquid extraction column 21.
- An extract 16 consisting mainly of solvent, inorganic extracts, compounds present in dilute biocrude 20, such as diluent 28 and biocrude 20. Aqueous effluent 16 in column 21, called extract, is an aqueous solution rich in inorganics, with the inorganics being used as catalysts for hydrothermal liquefaction. Extract 16 is sent to separation step 11 to recycle the inorganics to the hydrothermal liquefaction stage via stream 30.

[0108] Raffinate 25 feeds a separation device 26 based on boiling temperature, such as a distillation column, an evaporator, an exchanger followed by a flash separator flask. This device makes it possible to separate a "diluent" 28 (which can be recycled at an inlet of column 21), which consists of a light constituent or a mixture of light constituents, and a demineralized biocrude 27 with a greatly reduced content of inorganics, in particular metals, compared to biocrude 19.

[0109] The invention achieves a reduction (by weight) of the content of inorganic compounds, such as mineral salts / metal salts, of at least 50% (by weight) and in particular by at least 70% (by weight). Biocrude grades can be achieved with levels of up to 500 ppm, including no more than 400 or 300 or 200 or 100 ppm of all these inorganic compounds.

[0110] It can be seen that when the process of treating the biocrude to reduce its content of inorganic/mineral compounds (especially metallics) is integrated into the hydrothermal liquefaction process, it consumes no (or much less) water, and the extracted inorganic compounds can be recycled in hydrothermal liquefaction as catalysts and chemicals. These two advantages make it possible to reduce the overall operating cost of the two combined processes.

Examples

Example 1 according to the state of the art

[0111] A hydrothermal liquefaction unit, the features of which are described below, produces a biocrude which is then sent to another site to be demineralized by liquid-

liquid extraction.

[0112] The charge of the hydrothermal liquefaction unit is woody biomass. The operating conditions for hydrothermal liquefaction are:

- temperature T : between 200 and 400°C (typically between 350 and 400°C, for example around 375°C)
- pressure P: between 5 and 400 MPa (typically comprised between 30 and 40 Mpa, for example around 35 MPa)
- alkaline cations (e.g., Na⁺ and K⁺) : introduced in form of catalyst and pH adjuster, typical consumption data are between 1 and 20 grams of alkaline cations per kg of (dry) biomass, notably 20 g of sodium per kg woody biomass (dry) and 10 g of potassium per kg biomass (dry).

[0113] The biocrude obtained at the outlet of the hydrothermal liquefaction unit has a dynamic viscosity at 20°C of 142 cP, a density at 15°C of 985 kg/m³ and contains 912 ppm weight of sodium Na, 640 ppm weight of potassium K and 30 ppm weight of calcium Ca.

[0114] This biocrude is sent to an inorganic reduction unit (demineralization) that is located at another site away from the hydrothermal liquefaction site.

[0115] In the inorganic reduction unit, the biocrude is diluted with a light fraction of the biocrude having a final boiling point below 150°C, this fraction is obtained by distillation of the diluted biocrude after liquid-liquid extraction. The mass flow rate of biocrude is 200 kg/h and the mass flow rate of the light fraction of biocrude is 200 kg/h.

[0116] The dilute biocrude has a mass flow rate of 400 kg/h, a dynamic viscosity at 20°C of 1.7 cP and a density at 15°C of 890 kg/m³.

[0117] The diluted biocrude feeds a counter-stream liquid-liquid extraction column agitated and operated at 40°C under 1 atm. The dispersed phase is the light phase (dilute biocrude). The diluted biocrude feeds the liquid-liquid extraction column at its bottom.

[0118] Demineralized water feeds the liquid-liquid extraction column at its head with a flow rate of 200 kg/h.

[0119] The liquid-liquid extraction column has an estimated theoretical number of stages of about 3 under the conditions of use presented.

[0120] The product coming out at the bottom of the liquid-liquid extraction column, called extract and rich in inorganics, is sent to a water treatment section before being discharged.

[0121] The product coming out at the head of the liquid-liquid extraction column 21, called raffinate 25, is distilled in a distillation column 26. At the head of the distillation column, a light fraction of biocrude 28 is obtained, which is remixed with fresh biocrude rich in inorganics 19 in order to reduce its density and viscosity before liquid-liquid extraction.

[0122] At the bottom of the distillation column 26, a demineralized biocrude 27 is obtained, which contains

only 3 ppm weight of sodium, 1 ppm weight of potassium and 7 ppm weight of calcium. The water consumption to reduce the inorganics of the biocrude is 200 kg/h of demineralized water.

[0123] The hydrothermal liquefaction unit needs 12 kg/h sodium (as Na⁺) and 6 kg/h potassium (as K⁺) for a 200 kg/h biocrude production.

Example 2 according to the invention

[0124] The same hydrothermal liquefaction unit as in Example 1 is used to produce biocrude, but here the inorganic reduction unit is integrated into the hydrothermal liquefaction unit, i.e., the two units are close together and exchange several streams with each other.

[0125] The same biocrude as in example 1 is obtained at the outlet of the hydrothermal liquefaction unit.

[0126] The biocrude is diluted with a light fraction of the biocrude having a final boiling point below 150°C, this fraction is obtained by distillation of the diluted biocrude after liquid-liquid extraction. The mass flow rate of biocrude is 200 kg/h and the mass flow rate of the light fraction of biocrude is 200 kg/h.

[0127] The dilute biocrude has a mass flow rate of 400 kg/h, a dynamic viscosity at 20°C of 1.7 cP and a density at 15°C of 890 kg/m³.

[0128] The diluted biocrude feeds a counter-stream liquid-liquid extraction column 21 agitated and operated at 40°C under 1 atm. The dispersed phase is the light phase (dilute biocrude 20). The diluted biocrude feeds the liquid-liquid extraction column 21 at its bottom.

[0129] The liquid-liquid extraction column 21 is fed at its head by 200 kg/h of aqueous phase obtained by condensation of vapors from separator 11 of the hydrothermal liquefaction unit.

[0130] The liquid-liquid extraction column 21 has an estimated number of theoretical stages of the order of 3 under the operating parameters presented above.

[0131] The product coming out at the bottom of the liquid-liquid extraction column 21, called extract 16 and rich in inorganics, is sent to separator 11 of the hydrothermal liquefaction unit. The inorganics extracted from the biocrude are thus recycled during hydrothermal liquefaction and thus reduce the amount of fresh catalysts and chemicals to use (in particular Na, K compounds).

[0132] The product coming out at the head of the liquid-liquid extraction column 21, called raffinate 25, is distilled in a distillation column 26. At the head of the distillation column, a light fraction of biocrude 28 is obtained, which is remixed with fresh biocrude rich in inorganics 19 in order to reduce its density and viscosity before liquid-liquid extraction in column 21.

[0133] At the bottom of the distillation column 26, a demineralized biocrude 27 is obtained, which contains only 3 ppm weight of sodium, 1 ppm weight of potassium and 7 ppm weight of calcium.

[0134] In this example, no water is consumed to reduce the inorganics of the biocrude and the consumption of

sodium and potassium for hydrothermal liquefaction is reduced by 3%.

[0135] The invention therefore makes it possible to drastically reduce the mineral compound content of the biocrude, while considerably reducing the utility consumption of the overall liquefaction + treatment process.

Claims

1. Process for hydrothermal liquefaction of an initial carbon feedstock (1) at least partly derived from biomass, in order to obtain a so-called biocrude product with a reduced content of mineral compounds (27), said process comprising the following steps:

- step (a) mixing the initial carbon filler (1) with at least one catalyst and at least one liquid phase, including at least a first aqueous phase (30) containing all or part of the catalyst and optionally at least a first organic phase (4,2),
- step b) of hydrothermal liquefaction (5) of the mixture (3) obtained in step a), in order to obtain a liquefaction product (7),
- step c) of liquid/ liquid/gas separation(8) of the liquefaction product (7) obtained in step (b), in order to obtain a first gaseous phase (31), a second liquid aqueous phase (10) and a second liquid organic phase (18) known as a biocrude,
- step (d) of separation by heating of the second aqueous phase (10) obtained in step (c), in order to obtain a third liquid aqueous phase (12) enriched with minerals from at least the catalyst used in step (a) of mixing, and a first phase of water vapor (22),
- step (e) of dilution of the second liquid organic phase (18) called biocrude obtained in step (c) with a diluent (28) comprising an organic liquid phase which has a lower viscosity and density than those of said second liquid organic phase called biocrude, so as to obtain a dilute biocrude (20),
- a step (f) of contacting the dilute biocrude (20) obtained in step (e) with at least one solvent (17,23,24) comprising a liquid aqueous phase, with counter-stream liquid-liquid extraction, so as to obtain, on the one hand, a raffinate (25) comprising the biocrude depleted in mineral compounds and diluent, and, on the other hand, an extract (16) comprising the solvent enriched with mineral compounds,
- a step (g) of separation of the raffinate (25) obtained in step f) of contact, so as to obtain, on the one hand, the biocrude depleted in mineral compounds (27) and on the other hand a phase (9,28) comprising the diluent,
- a step (h) of condensation of a first part of the

- first vapor phase (22) obtained in step (d) and recycling of said part of the first steam phase when condensed as a solvent (17) in contacting step (f);
- a step (i) of at least partial recycling of the extract (16) obtained in contacting step (f) to step (d) of separation by heating;
 - a step (j) of separation of a second part of the first vapor phase (22) obtained in step (d), in order to obtain a fourth aqueous phase (15), and a first organic phase called light phase (2).
2. A process according to the preceding claim, **characterized in that** the first so-called light organic phase (2) obtained in step (j) is at least partly recycled as the first organic phase in mixing step (a).
 3. A process according to one of the preceding claims, **characterized in that** at least part of the second liquid organic phase (18) called biocrude obtained in step (c) of liquid /liquid/gas separation is recycled as the first organic phase (4) in mixing step (a).
 4. A process according to one of the preceding claims, **characterized in that** it comprises a step k) of at least partial recycling of the phase comprising the diluent (28) obtained in step (g) of separation as a diluent in step (e) of dilution.
 5. A process according to one of the preceding claims, **characterized in that** it comprises a step (l) of at least partial recycling of the phase comprising the diluent (28) obtained in step (g) of separation in step (c) of liquid /liquid/gas separation (8).
 6. A process according to one of the preceding claims, **characterized in that** it comprises a step (m) of at least partial recycling of the third liquid aqueous phase (12) toward mixing step (a).
 7. A process according to one of the preceding claims, **characterized in that** step (b) of hydrothermal liquefaction comprises heating, at a temperature between 250°C and 450°C under a pressure between 100.10⁵ Pa and 350.10⁵ Pa, in the presence of at least one catalyst containing a pH modifying component and/or an alkaline, such as Na or K and/or an alkaline earth such as Ca.
 8. A process according to one of the preceding claims, **characterized in that**, in step (e) of dilution, the diluent (28) has a final boiling point of at most 150°C, preferably of at most 100°C.
 9. A process according to one of the preceding claims, **characterized in that**, at the end of step (e) of dilution, the dilute biocrude (20) has a dynamic viscosity at 20°C of at most 7 cP, preferably of at most 4 cP, and a density at 15°C of at most 950 kg/m³, of at most 900 kg/m³.
 10. A method according to one of the preceding claims, **characterized in that**, in step (e) of dilution, the ratio R of the flow rate Qd of the diluent (28) to the flow rate Qb of the biocrude (19) is of at most 10, and in particular at least 0,1, the ratio R being preferably between 0.5 and 3.
 11. A method according to one of the preceding claims, **characterized in that** the contact step (f) is carried out at a temperature between 15 and 150°C and below the boiling point of the diluent (28) at the contact pressure, and at a contact pressure between 0.5.10⁵ Pa and 15.10⁵ Pa.
 12. A process according to one of the preceding claims, **characterized in that** step (d) of separation and/or step (g) of separation and/or step (j) of separation is a treatment comprising at least evaporation, distillation, heating followed by separation.
 13. A process according to one of the preceding claims, **characterized in that** the diluent (28) used in step (e) of dilution is selected from a light cut present in the biocrude feedstock or a chemical compound or mixture of chemical compounds, in particular of the family of alcohols, ethers, ketones and hydrocarbons.
 14. A method according to one of the preceding claims, **characterized in that** the solvent (17,23,24) used in contacting step (f) is selected from at least one of the following solutions: a pure aqueous solution, a demineralized aqueous solution, an aqueous solution containing soluble organic compounds, an acidic aqueous solution.
 15. A method according to one of the preceding claims, **characterized in that** step (f) of contact is followed by step (f1) and/or (f2) of settling.
 16. A method according to one of the preceding claims, **characterized in that** step (f) of contacting the dilute biocrude (20) obtained in step (e) is carried out with at least two separate solvents (24,17) which are brought into contact with said dilute biocrude (20) in separate contact zones and comprising a first solvent which is an aqueous liquid phase with a neutral pH, between 6.5 and 7.5, and a second solvent which is an acidic aqueous liquid phase, with a pH of less than 6.5.
 17. Facility for the hydrothermal liquefaction of an initial carbon filler at least partly derived from biomass, in order to obtain a so-called biocrude product with a reduced content of mineral compounds (27), the

said facility comprising the following devices :

- a device (a) for mixing the initial carbon feed-stock (1) with at least one catalyst and at least one liquid phase, including at least a first aqueous phase (30) containing all or part of the catalyst and optionally at least a first organic phase (4,2), 5
- a device (b) for hydrothermal liquefaction of the mixture (3) obtained with the mixing device (a), 10
- a liquid/liquid/gas separation device (c) for the liquefaction product (7) obtained in step (b), in order to obtain a first gaseous phase (31), a second liquid aqueous phase (10) and a second liquid organic phase (18) called biocrude, part of which (4) may be recycled as an organic phase in the mixing device (a), 15
- a device (d) for separating by heating the second liquid aqueous phase (10) obtained with the liquid/liquid/gas separation device (c) in order to obtain a third liquid aqueous phase (12) enriched with minerals derived from at least the catalyst used in the mixing device (a) and a first phase of water vapor (22), 20
- a device (e) for diluting the second liquid organic phase (18) called biocrude obtained with the device (c) for liquid/liquid/gas separation with a diluent (28) comprising an organic liquid phase which has a viscosity and density lower than that of said second liquid organic phase called biocrude, so as to obtain a dilute biocrude (20), 25
- a device (f) for contacting the dilute biocrude (20) obtained with the dilution device (e) with at least one solvent (17,24) comprising a liquid aqueous phase, said device comprising a counter-stream liquid-liquid extraction column (21), preferably gravity-driven, so as to obtain, on the one hand, a raffinate (25) comprising the biocrude depleted in mineral compounds and diluent, and, on the other hand, an extract (16) comprising the solvent enriched with mineral compounds, 30
- a device (g) for separating the raffinate (25) obtained with the contacting device (f), so as to obtain, on the one hand, the biocrude depleted in mineral compounds (27) and, on the other hand, a phase comprising the diluent (28), 35
- a device (h) for condensing part of the first vapor phase (22) obtained in step (d) and recycling said part of the first vapor phase once condensed as a solvent (17) in contacting step (f), 40
- a device (i) for recycling at least part of the extract (16) obtained with the contacting device (f) towards the device (d) for separation by heating, 45

- (j) a device for separating at least a second part of the first vapor phase (22) obtained in step (d), in order to obtain a fourth aqueous phase (15), and a first so-called light organic phase (2) possibly recycled as an organic phase in the mixing device (a).

18. A facility according to the preceding claim, **characterized in that** it comprises a device (k) for recycling at least part of the phase comprising the diluent (28) obtained with the separation device (g) as a diluent in dilution step (e).
19. A facility according to one of claims 17 or 18, **characterized in that** it comprises a device (l) for recycling at least part of the phase comprising the diluent (9) obtained with the separation device (g) towards the device (c) for liquid /liquid/gas separation (8).
20. A facility according to one of claims 17 to 19, **characterized in that** it comprises a device (m) for at least partial recycling of the liquid third aqueous phase (12) towards the mixing device (a).
21. A facility according to one of claims 17 to 20, **characterized in that** the device (d) for separating (11) by heating the second liquid aqueous phase (10) and/or the separation device (g) (26) and/or the separation device (j) comprises at least one device selected from a distillation column, an evaporator, an exchanger followed by a separator flask, in particular a separator device said "flash".
22. A facility according to one of claims 17 to 21, **characterized in that** it comprises a recycling device of at least part of the phase (28) comprising the diluent obtained with the separation device (g) as a diluent for the dilution device (e).
23. A facility according to one of claims 17 to 22, **characterized in that** the contacting device (f) comprises a counter-stream liquid/liquid extraction column (21), preferably gravity-driven, and preferably equipped at the bottom of the column and/or at the head of the column with a settling device (f1) and/or (f2).

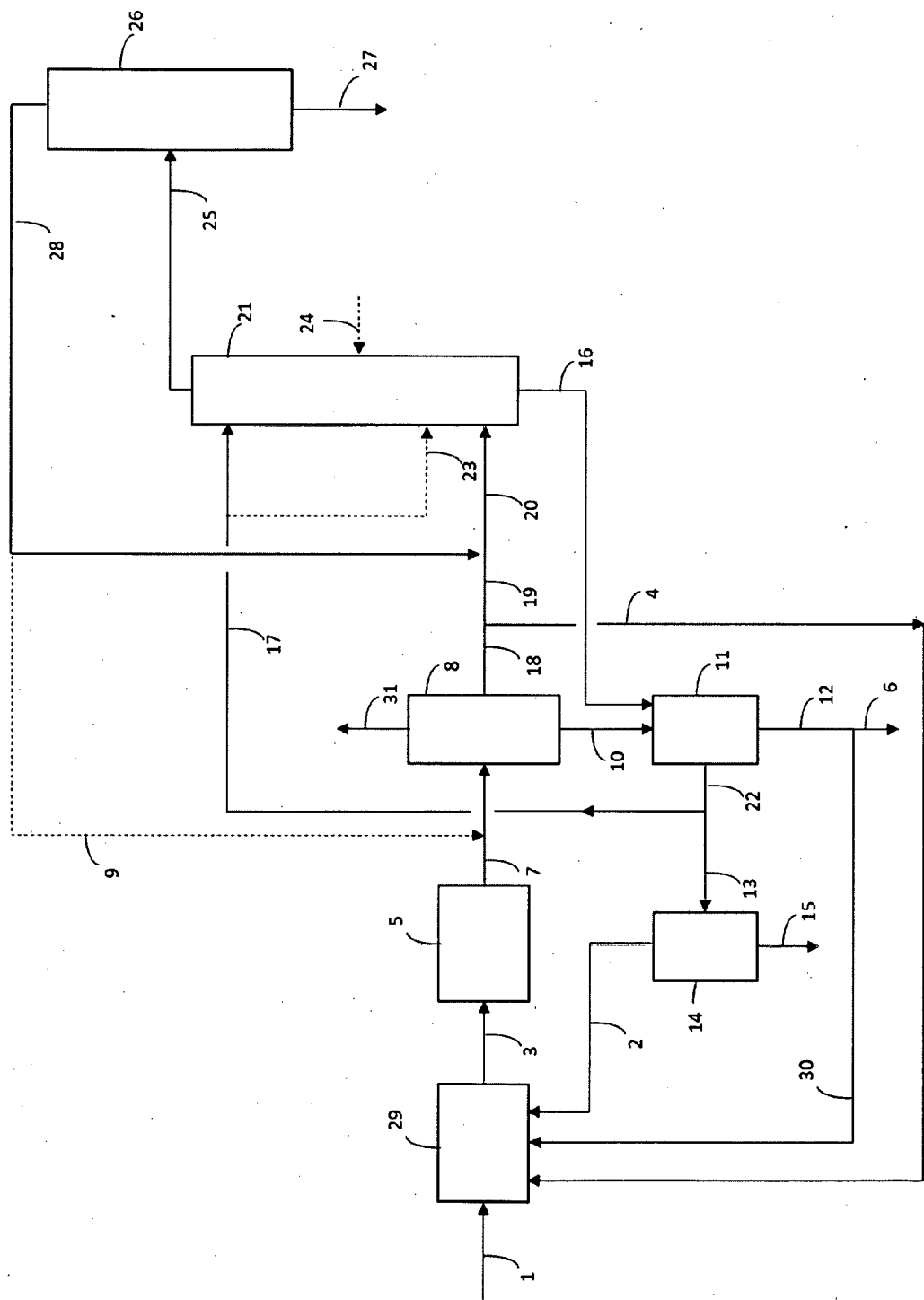


FIG.1



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