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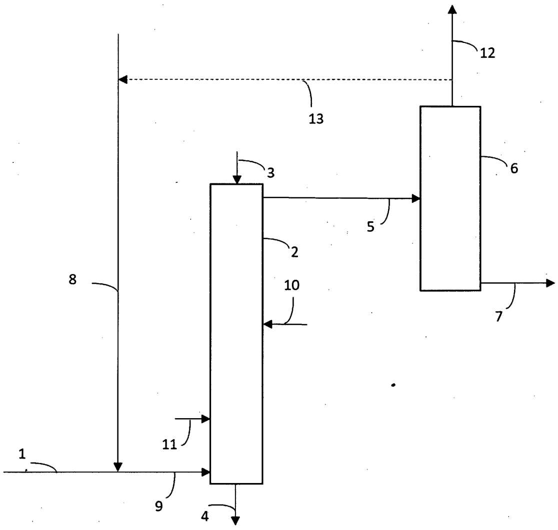
(54) PROCESS FOR TREATING A CARBONACEOUS LIQUID FEEDSTOCK FROM A HYDROTHERMAL LIQUEFACTION TREATMENT

(57) The invention relates to a method of treating a feedstock from a hydrothermal liquefaction treatment with a view to reducing its mineral content, with
- a step (a) diluting the biocrude with a diluent (8,12) which comprises an organic liquid phase so as to obtain a diluted biocrude (9),
- a step (b) of contacting the dilute biocrude (9) obtained in step (a) with two separate solvents which are brought into contact with said feedstock in separate contact zones (3;7) and comprising a first solvent (3) which is an aqueous liquid phase with neutral pH and a second solvent (10) which is an acidic aqueous liquid phase, with counter-current liquid-liquid extraction, so as to obtain a raffinate (5) comprising the depleted mineral and diluent feedstock, and an extract (4) comprising the enriched solvent s in mineral compounds,
- a step (c) of separation of the raffinate (5) obtained in step (b), so as to obtain a biocrude depleted of mineral compounds (11) and a phase comprising the diluent (8,12).

[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 "HydroThermal Liquefaction", which make it possible to transform biomass into a carbon feedstock called "biocrude". This so-called "biocrude" feedstock 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 feedstock in the presence of water at a pressure between 100 and 350 bar (between 10^7 Pa and 3.5×10^7 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.

[0003] 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.

[0004] 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 quite 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.

[0005] 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.

[0006] The yields 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 biocrude and of gas of 40-45% as well.

[0007] 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, used tires. The feedstock can also be a mixture of two or more of these materials.

[0008] 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 feedstock, the biocrude contains compounds from cellulose, hemicellulose, and lignin (the structure found in lignocellulosic biomass).

[0009] The biocrude obtained by hydrothermal liquefaction has an oxygen, sulfur and nitrogen content that varies 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).

[0010] 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.

[0011] 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.

[0012] 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 alkali or alkaline earth metals such as Na, K, Ca, etc.). These metals poison the catalysts: they deactivate them at least partially.

[0013] 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 conducted.

[0014] It is known from patent applications WO18177877, WO19092173, WO21121662 treatments aimed at purifying biocrudes, and in particular at recovering the metal salts they contain for recycling, with different types of separation devices, using acidic aqueous phases or washing agents, but the implementations of these separation/treatment operations seem complex.

[0015] The aim of the invention is to develop a treatment to reduce the content of mineral compounds, in particular metallics, of a biocrude-type feedstock, a treatment that is preferably simple to implement, and preferably economical in terms of tools and/or utility consumption.

Summary of the invention

[0016] The invention first relates to a method for treating a liquid feedstock comprising at least partly carbonaceous products and resulting from a hydrothermal liquefaction treatment, known as biocrude (feedstock), with a view to reducing the content thereof of mineral compounds, in particular metallic compounds, such as said treatment comprises

- a step a) of dilution of the biocrude feedstock with a diluent comprising an organic liquid phase which has a viscosity and a density lower than that of the biocrude feedstock, so as to obtain a dilute biocrude,
- a step b) of contacting the dilute biocrude obtained in step a) 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, with counter-current liquid-liquid extraction, so as to obtain, on the one hand, a raffinate comprising the biocrude depleted in mineral compounds and the diluent, and, on the other hand, an extract comprising the enriched solvent s in mineral compounds,
- a step c) of separation of the raffinate obtained in step b), so as to obtain, on the one hand, the biocrude depleted in mineral compounds, and on the other hand, a phase comprising the diluent.

[0017] Thus, the invention succeeds in significantly reducing the mineral compound content of a biocrude-type feedstock, the reduction being sufficient to allow the subsequent processing steps of such a feedstock to be carried out without having to modify its conventional operation, in particular by maintaining the type of catalyst usually used for these steps of hydroconversion, hydrotreating, hydrocracking, or catalytic cracking type.

[0018] And to do this, the invention first uses a dilution with a "light" organic diluent (less dense and less viscous than biocrude), then a liquid/liquid counter-current extraction with two different solvents, put in contact with the diluted biocrude in different zones. One method of implementation that will be described later is to use a liquid/liquid extraction column (or several in series and/or parallel), in particular a gravity-type column, and differentiating the injection points of the different solvents, at different column heights in particular. And it turned out that this combination of dilution + extraction with two different solvents with differentiated contact is very efficient.

[0019] Conducting an extraction in such a liquid/liquid extraction column requires a sufficient difference in density between the different phases, in this case between the dilute biocrude on the one hand, and the two solvents on the other hand (difference often greater than 50 kg/m^3), and the greater the difference in density, the easier the implementation of the extraction. 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-current columns are interesting because they allow the desired solutes to be extracted much better than in a co-current 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. Using two different contact injection points/solvents has surprisingly proven to be very interesting in greatly improving the efficiency of the extraction.

[0020] Preferably, the first solvent S1 is chosen from pure water, demineralized water, water with soluble organic molecules.

[0021] Preferably, the second solvent S2 is an acidic aqueous solution, having a pH of less than 6.5.

[0022] Advantageously, the second solvent S2 is an acidic aqueous solution containing from 10 ppm (in particular from100 ppm) to 20% weight of at least one strong or weak acid, organic or mineral, in particular chosen 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.

[0023] The second solvent may also be an aqueous solution acidified by injecting carbon dioxide into the aqueous solution (which may already contain at least one of the above-mentioned acids). Indeed, the hydrothermal liquefaction step prior to the treatment according to the invention tends to generate carbon dioxide, which can therefore be advantageously used to acidify the solvent in question.

[0024] In contacting step b), the ratio R_1 of the flow rate of the first solvent Q_{s1} to the flow rate of the dilute biocrude feedstock Q_m is preferably between 0.05 and 5, preferably between 0.1 and 3.

[0025] in contacting step b), the ratio R_2 of the flow rate of the second solvent Q_{s2} to the flow rate of the dilute biocrude feedstock Q_m is preferably between 0.05 and 5, preferably between 0.1 and 3.

[0026] Preferably, contact step b) includes dedicated or additional settling (decantation), to improve the settling (decantation) between the two aqueous and organic phases. The settling device used (e.g., a decanter) may be located after one extraction column or after 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). 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 raffinate. In this case, a decanter can be placed downstream to better separate the water (and not upstream of the column). If the contacting 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).

[0027] The method according to the invention may also comprise:

- a step (d) of recycling at least part of the phase comprising the diluent obtained in step c) as a diluent in dilution step (a).

[0028] This recycling can be partial or total: it can be supplemented by an external diluent, if necessary, but it is very interesting, because it allows to drastically reduce the diluent consumption of the process.

[0029] Advantageously, the method of the invention may also comprise: ’

- a step e) of processing the extract obtained in contacting step b) to reduce its mineral content,
- a step f) recycling of at least a portion of the extract with reduced mineral content obtained in step e) as a solvent in contacting step b). Again, this extract can therefore be at least partially recycled, preferably by purifying it beforehand, to replace all or part of at least one of the (aqueous) solvents used during the liquid /liquid extraction, which also reduces the water consumption of the process according to the invention.

[0030] Step e) allows also to recover these mineral compounds, e.g., metal salts, for recycling.

[0031] Preferably, in dilution step a), the diluent has a final boiling point of not more than 150°C, preferably not more than 100°C.

[0032] Preferably, the diluent used in dilution step a) is selected from a light cut present in the feedstock of or a chemical compound or mixture of chemical compounds, including alcohols, ethers, ketones and hydrocarbons. Advantageously , the process can be started with a solvent boiling temperature close to that of the cut to be recycled, then the light cut will accumulate in the loop over time, because it is recycled (by distillation), and it will gradually replace the initial solvent.

[0033] Preferably, at the end of dilution step a), 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/m^3, preferably at most than 900 kg/m^3.

[0034] Preferably, in dilution step a), the ratio R of the flow rate Qd of the diluent to the flow rate Qb of the biocrude feedstock is at most 10, and in particular at least 0.1, with the ratio R preferably between 0.5 and 3.

[0035] Preferably, contacting step b) is conducted at a temperature between 15°C and 100°C, while remaining below the boiling temperature of the diluent, and at a pressure between 0.5 10^5 Pa and 5. 10^5 Pa.

[0036] Preferably, separation step c) is a treatment consisting of at least evaporation, distillation, heating followed by separation.

[0037] The invention also relates to a treatment facility for a liquid feedstock comprising at least partly carbonaceous products and resulting from a hydrothermal liquefaction treatment, known as biocrude, with a view to reducing its content in mineral compounds, in particular metallic compounds, and which implements the process as described above.

[0038] The invention also relates to a facility for the treatment of a liquid feedstock comprising at least partly carbonaceous products and resulting from a hydrothermal liquefaction treatment, known as biocrude, with a view to reducing the content thereof of mineral compounds, in particular metallic compounds, such as said facility comprises

- a device (a) for diluting the biocrude with a diluent comprising an organic phase which has viscosity and density lower than those of the biocrude, so as to obtain a dilute biocrude
- a device (b) for contacting the dilute biocrude obtained in step (a) with at least two separate solvents, 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, said device comprising a counter-current liquid-liquid extraction column, preferably gravity-driven, the first and second solvents having separate inlets and are arranged at

different heights of the column, so as to obtain, on the one hand, a raffinate comprising the biocrude depleted in mineral compounds and the diluent, and, on the other hand, an extract comprising the solvents enriched with mineral compounds

- a device (c) for separating the raffinate obtained with the contacting device (b), so as to obtain, on the one hand, the biocrude feedstock depleted in mineral compounds, and on the other hand a phase comprising the diluent.

[0039] The facility according to the invention therefore combines a dilution device with a "light" organic diluent (less dense and less viscous than biocrude), and (at least) a liquid/liquid counterflow extraction column with two different solvents, at different injection points. Preferably, at least one of the solvents is injected at the head of the column while the other solvent is injected at an intermediate column height, and the dilute biocrude is injected at the bottom of the column.

[0040] According to one variant, at least one of the first and second solvents has at least two separate inlets arranged at different heights of the column. Thus, one of the solvents may have two different injection points (injection inlets), at different column heights, e.g., one injection point at the head of the column and (at least) another at an intermediate column height, or two injection points at different intermediate column heights .

[0041] For example, at least one of the inlets of the first solvent may be at the head of the column.

[0042] It is also possible that one of the inlets of the second solvent is at the head of the column.

[0043] 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 H_2 with respect to the total height H of the column such that the ratio H_2/H is between 0.2 and 0.8.

[0044] It is also possible that it is rather one of the inlets of the first solvent that is at an intermediate height of the column, especially at the height H_2 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.

[0046] If the first solvent (or the second solvent) has a second inlet in the column at an intermediate height H_3, then this intermediate height H_2 is preferably less than the height H_2 of the inlet of the second solvent (or first solvent).

[0047] Advantageously, this height H_3 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 H_3/H is between 0.05 and 0.4.

[0048] The contacting device is preferably a liquid/liquid extraction column with gravitational counterflow. It can be a single column or a plurality, mounted in series or in parallel. The column(s) can be equipped at the top and/or bottom of the column with settling devices.

[0049] The dilution device can be a tank-type device fed by both the biocrude 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 conducted dynamically towards the contacting device, using appropriate valves.

[0050] For example, the separation device is at least one device chosen from: a distillation column, an evaporator, an exchanger followed by a separator tank, in particular a so-called "flash" separator tank.

[0051] The facility according to the invention may also comprise a recycling device of at least part of the phase comprising the diluent obtained with separation device c) as’a diluent for the dilution device a). This recirculation device may consist of pipe(s) providing a fluidic connection between the two devices a) and c) and controlled in a known manner by valves.

[0052] 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, preferably, a treatment for converting the treated biocrude such as hydroconversion, hydrotreating, hydrocracking, catalytic cracking in order to produce biofuels and/or other chemical compounds (so-called bio-based compounds).

List of Figures

[0053]

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

Figure 2: This figure shows in a very schematic way a variant of the facility implementing the biocrude treatment process according to the invention shown in Figure 1.

[0054] This figure does not therefore represent all the equipment in the installation, but those which are most useful for the understanding of the invention. The different devices and others are not necessarily to scale, nor necessarily represented in space as they can be in an industrial site.

[0055] The same reference numerals correspond to the same devices /streams from one figure to the other.

Description of embodiments

[0056] The invention aims to treat biocrude-type feedstocks in order to reduce the content of mineral compounds thereof, particularly metallics.

[0057] As a reminder, the characteristics of a biocrude-type feedstock of interest to the invention may be as follows: 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.

[0058] In the case of a lignocellulosic biomass load, the biocrude contains compounds from cellulose, hemicellulose, and lignin (structure present in lignocellulosic biomass).

[0059] 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).

[0060] 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 feedstock, and from metals used to grind the hydrothermal liquefaction feedstock. Sodium and potassium can be present in significant quantities in the biocrude because the hydrothermal liquefaction process uses alkali-based catalysts (NaOH, KOH, K_2CO_3, Na_2CO_3, etc.) in significant quantities.

[0061] 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.

[0062] 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% of the biocrude is vaporized in the range 180-350°C and 45% weight to 80% weight of the biocrude is vaporized above 350°C.

[0063] Figure 1 shows a facility for implementing the invention, which will be described below. Biocrude 1 from the hydrothermal liquefaction unit has a flow rate of Qb. Biocrude 1 is mixed with diluent 8 with a flow rate of Qd such as $0.1 < Qd/Qb < 10$ and preferably $0.5 < Qd/Qb < 3$. Flow rates are measured in mass per unit of time. Diluent 8 is a compound or mixture of compounds with a dynamic viscosity at 20°C of less than 4 cP and a density at 15°C between 600 and 850 kg/m^3. The dilution is operated by providing in the supply pipe conveying the biocrude 1 to the extraction column 2 with a pipe bringing the diluent: the mixture between the biocrude and the diluent is implemented in the common pipe portion downstream of the tapping. ("upstream" and "downstream" are understood in this text by considering the progression of the biocrude in the facility).

[0064] Mixture 9, biocrude + diluent, called "dilute biocrude", has 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/m^3, preferably less than or equal to 900 kg/m^3 at atmospheric pressure (and for example at least 600 kg/m^3 at atmospheric pressure) . These properties are obtained by choosing an appropriate diluent type and diluent flow rate (in relation to the biocrude flow rate).

[0065] Diluent. 12 may be a light cut present in the biocrude, accumulated in the recycling loop over time (as seen later with Figure 2), or it may be a chemical compound (or 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.

[0066] The final boiling point of diluent 12 is preferably less than or equal to 150°C, and preferably less than or equal to 100°C, and preferably of at least 60°C.

[0067] The dilute biocrude 9 feeds a liquid-liquid extraction column, called gravity column, 2 at its bottom with a given mass flow rate Qm. Column 2 extends along a vertical or essentially vertical longitudinal axis.

[0068] The liquid-liquid extraction is conducted according to the invention using two different solvents S1 and S2, injected at different injection points in column 2: (the invention can also be carried out with more than two different solvents):

> Solvent S1 consists of an aqueous solution with a neutral pH ($6.5 < pH < 7.5$), which can be pure water, demineralized water, water with soluble organic molecules.
> Solvent S2 consists of 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. Solvent S2 may also contain soluble organic molecules.

[0069] The solvent S1 feeds column 2 with current 3, at the head of the column. The flow rate Qs1 of current 3 is chosen such as $0.05 < Qs1/Qm < 5$ and preferably $0.05 < Qs1/Qm < 3$.

[0070] The solvent S2 feeds column 2 with current 7, in the intermediate position in column 2.

[0071] The Qs2 flow rate of current 7 is chosen such as $0.05 < Qs2/Qm < 5$ and preferably $0.05 < Qs2/Qm < 3$.

[0072] Flow rates are measured in mass per unit of time. It is also possible to reverse the injection points, and to inject solvent S2 with current 3 and solvent S1 with current 7.

[0073] The total usable height of column 2, H, 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.

[0074] With H_2 being the height between the column bottom (in its useful part) and the position of the current injection point 10, the ratio H_2/H is between 0.2 and 0.8.

[0075] According to a first (optional) variant of the invention, and as shown in Figure 1, the solvent S1 is injected partly at the head of the column via current 3, but also partly in the lower position, via current 6, with flow rate Qs1'.

[0076] With H_3 being the height between the column bottom (in its useful part) and the position of the injection point of current 6, the ratio H_3/H is between 0.05 and 0.4, and H_3 remains inferior to H : Injection point 6 is lower than-injection point 10.

[0077] Qs1' is chosen such as $0.05 < Qs1'/Qm < 5$, and preferably $0.05 < Qs17Qm < 3$.

[0078] The liquid-to-liquid extraction column 2 has the following features:

- Operating pressure P between 0.5 bar abs ($0.5.10^5$ Pa) and 15 bar abs (15.10^5 Pa), preferably between 0.9 bar abs ($0.9.10^5$ Pa) and 1.5 bar abs ($1.5.10^5$ Pa).
- Operating temperature T between 15°C and 15 0°C, preferably between 20°C and 60°C
- F/S between 5 and 80 m/h, preferably between 10 and 40 m/h with:

  S is the cross-section of column 2, in m^2
  F is the total volume traffic in column 2, where F is defined as follows:

$$F = Qm/rhom + (Qs1 + Qs1')/rhos1 + Qs2/rhos2, \text{ expressed in } m^3/l$$

  expressed in m^3/h
  rhom, rhos1 and rhos2 being the respective densities of dilute biocrude 9, solvent S1 and solvent S2 under the operating conditions of column 2 (pressure, temperature)

[0079] In column 2, two phases are mixed and brought into contact: an organic phase (dilute biocrude 9) and an aqueous phase (solvent S1 and solvent S2). In column 2, one phase is dispersed into the other, which is the continuous phase.

[0080] 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.

[0081] The dispersed phase can be the heavy phase (solvent 3, solvent 7) or the light phase (dilute biocrude 9), but preferably the light phase (dilute biocrude 9). If the dispersed phase is the heavy phase (solvent 3, solvent 7), column 2 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 9). It is also possible to provide a decanter at the bottom and at the head of the column.

[0082] The column allows to reach a theoretical number of stages between 2 and 15, and preferably between 2.5 and 7.

[0083] The effluents in column 2 are:

- A raffinate 5 consisting mainly of biocrude, diluent and compounds present in solvents (mainly water). The amount of inorganics present in raffinate 5 is much lower than in dilute biocrude 9, due to the efficiency of liquid-liquid extraction.
- An extract 4 consisting mainly of solvents S1 and S2, extracted inorganics, compounds present in dilute biocrude 9, such as diluent and biocrude.

[0084] Raffinate 5 feeds a separation device 10 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" 8 which is made up of a light constituent or a mixture of light constituents, and a demineralized biocrude 11 with a greatly reduced content of inorganics, particularly metals, compared to biocrude 1.

[0085] In this way, at least 70% of the mineral content of biocrude can be reduced, in particular so as to reach a maximum mineral content (their sum) of no more than 500 ppm, in particular of no more than 400 or 300 or 200 or 100 ppm, which is remarkable.

[0086] Figure 2 represents a variant of the installation in Figure 1: the difference from the installation in Figure 1 is that at least a portion of phase 8 containing the diluent from contact step b) is recycled as diluent for dilution step a). In this way, diluent consumption of the process can be greatly reduced.

[0087] According to a third variant of the method according to the invention (possibly combined with at least one of the first and second variants), not shown in Figures, one of the two solvents, namely solvent S1 or solvent S2 (flow 3 and possibly flow 6 and/or 10) may come from the recycling of extract 4, if extract 4 has previously been treated to reduce its inorganic content (e.g. by evaporation). In this way, the water consumption of the process can also be significantly reduced.

[0088] Note that in the recycling of any stream contemplated in the context of the present invention, the stream may be only partially recycled, and the recycled stream may be supplemented by a stream of similar external composition (e.g., a water input in the recycling of extract 4 as a solvent, or an organic phase input in the recycling of stream 8 as a diluent).

Examples

Comparative example 1 (state of the art)

[0089] A biocrude derived from hydrothermal liquefaction of lignocellulosic biomass has a dynamic viscosity at 20°C of 142 cP and a density at 15°C of 985 kg/m^3. Biocrude contains several inorganics, also known as mineral compounds, including sodium Na, potassium K and calcium Ca. The sodium concentration is 912 ppm weight, the potassium concentration is 640 ppm weight, and the calcium concentration is 30 ppm weight.

[0090] The biocrude is diluted with 2-butanone (or methyl ethyl ketone, or MEK) with a MEK/biocrude mass ratio of 1 to reduce density and viscosity. MEK has a density at 15°C of 805 kg/m^3 and a dynamic viscosity at 20°C of 0.42 cP. MEK has a boiling point of 79.6°C. The dilute biocrude has a dynamic viscosity at 20°C of 1.7 cP and a density at 15°C of 890 kg/m^3.

[0091] A contacting test of biocrude diluted with acidic water is conducted in a 3 liter closed reactor with a dilute water/biocrude mass ratio equal to 0.5. Acidic water contains 0.1M citric acid. The engine, equipped with agitating means (propeller), is stirred at 500 rpm for 1 hour and then left to rest for 1 day. The reactor is operated at 40°C under 1 atm (10^5 Pa).

[0092] The decanted organic phase is separated and then distilled to separate the diluent from the demineralized biocrude. The analytical results of the demineralized biocrude indicate a sodium content of 33 ppm weight, a potassium content of 21 ppm and a calcium content of 10 ppm in the demineralized biocrude.

Example 2 according to the invention

[0093] The same diluted biocrude as in Example 1 is used to feed a Sulzer ECR type agitated counterflow liquid-liquid extraction column, with an internal diameter of 32 mm and a usable height of 1800 mm.

[0094] The operation is performed at 40°C under 1 atm (10^5 Pa). The column is agitated at a stirring speed of 90 rpm during operation.

[0095] The dispersed phase is the light phase (dilute biocrude). The diluted biocrude has a flow rate of 6 kg/h and feeds the column at its bottom.

[0096] Demineralized water is used as a solvent S1, and feeds the column at its head (flow 3) with a flow rate of 0.5 kg/h.

[0097] A 0.1M citric acid solution is used as an S2 solvent and feeds the column (flow 10) with a flow rate of 2.5 kg/h, at an injection point located in the middle of column 2 (900 mm high).

[0098] Column 2 has an estimated number of theoretical stages of the order of 3 under said conditions of use.

[0099] The organic phase thus treated and exiting at the top of extraction column 2 is distilled to separate the diluent from the demineralized biocrude. The analytical results of the demineralized biocrude indicate a sodium content of 3 ppm weight, a potassium content of 1 ppm and a calcium content of 7 ppm in the demineralized biocrude.

[0100] The sodium, potassium and calcium levels obtained with these two examples are compiled in Table 1 below:

Table 1

	Initial grades (biocrude 1)	Final grades Example 1 (demineralized biocrude)	Final grades Example 2 (demineralized biocrude 11)
Sodium Na content (ppm weight)	912	33	3
Potassium K content (ppm weight)	640	21	1
Calcium Ca content (ppm weight)	30	10	7

[0101] From the comparison of these two examples, it can be seen that with the method of the invention using a particular liquid-liquid extraction with two different aqueous solvents with counter-current flows is much more efficient than a simple contacting in a stirred reactor: with the invention it is possible to dramatically reduce the sodium content of the biocrude from 912 ppm to 3 ppm, that is, one can actually cut out almost all of the sodium. And this is also the case with potassium, and for calcium to a lesser extent.

Claims

1. Process for treating a liquid feedstock which comprises at least partly carbonaceous products and which is the result of a hydrothermal liquefaction treatment, known as biocrude feedstock (1), with a view to reducing the content of mineral compounds thereof, in particular metallic compounds, **characterized in that** said treatment comprises

- a step (a) dilution of the biocrude feedstock with a diluent (8, 12) comprising an organic liquid phase which has a viscosity and density lower than that of the biocrude feedstock, so as to obtain a dilute biocrude (9),
- a step (b) of contacting the dilute biocrude feedstock (9) obtained in dilution step (a) with at least two separate solvents which are brought into contact with said dilute biocrude in separate contact zones (3; (7) and comprising a first solvent (3) which is an aqueous liquid phase with a neutral pH, in particular between 6.5 and 7.5, and a second solvent (10) which is an acidic aqueous liquid phase, having a pH of less than 6.5, with counter-current liquid-liquid extraction, so as to obtain, on the one hand, a raffinate (5) comprising the biocrude feedstock depleted in mineral compounds and the diluent, and, on the other hand, an extract (4) comprising the solvents enriched with mineral compounds,
- a step (c) of separation of the raffinate (5) obtained in contacting step (b), so as to obtain, on the one hand, the biocrude depleted in mineral compounds (11), and, on the other hand, a phase comprising the diluent (8,12).

2. A process according to the preceding claim, **characterized in that** the first solvent (3) is selected from pure water, demineralized water, water with soluble organic molecules.

3. A process according to one of the preceding claims, **characterized in that** the second solvent (7) is an acidic aqueous solution having a pH of less than 6.5

4. A process according to one of the preceding claims, **characterized in that** the second solvent (7) is an acidic aqueous solution containing from 10 ppm to 20% by 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.

5. A method according to one of the preceding claims, **characterized in that**, in contact step (b), the ratio R_1 of the flow rate of the first solvent Q_{s1} to the flow rate of the dilute biocrude feedstock Q_m is between 0.05 and 5, preferably between 0. 1 and 3.

6. A method according to one of the preceding claims, **characterized in that**, in contacting step (b), the ratio R_2 of the flow rate of the second solvent Q_{s2} to the flow rate of the dilute biocrude feedstock (9) Q_m is between 0.05 and 5, preferably between 0.1 and 3.

7. A process according to the preceding claim, **characterized in that** it comprises

- a step (d) of recycling at least one (8) part of the phase comprising the diluent as a diluent in dilution step (a).

8. A process according to one of the preceding claims, **characterized in that** it comprises

- a step (e) of processing the extract (4) obtained in contacting step (b) to reduce its mineral content,
- a step (f) recycling of at least a part of the extract (4) with a reduced mineral content obtained in processing step (e) as a solvent (3) in contacting step (b).

9. A process according to one of the preceding claims, **characterized in that**, in dilution step (a), the diluent (8,12) has a final boiling point of at most 150°C, preferably at most 100°C.

10. A process according to one of the preceding claims, **characterized in that**, at the end of dilution step (a), the diluted biocrude (9) 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/m^3, preferably at most 900 kg/m^3.

11. A method according to one of the preceding claims, **characterized in that**, in dilution step (a), the ratio R of the flow rate Qd of the diluent (8,12) to the flow rate Qb of the biocrude feedstock (1) is at most 10, and in particular at least 0,1, the ratio R being preferably between 0.5 and 3.

12. A method according to one of the preceding claims, **characterized in that** the contacting step (b) is conducted at a temperature between 15°C and 100°C and at a pressure between $0.5.10^5$ Pa and 5.10^5 Pa.

13. A process according to one of the preceding claims, **characterized in that** step (c) of separation is a treatment comprising at least evaporation, distillation, heating followed by separation.

14. A process according to one of the preceding claims, **characterized in that** the diluent (8,12) used in dilution step (a) 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.

15. A facility for the treatment of a liquid feedstock comprising at least partly carbonaceous products resulting from a hydrothermal liquefaction treatment, known as a biocrude feedstock, with a view to reducing the content of mineral compounds thereof, in particular metallic compounds, **characterized in that** the facility comprises

- (a) a device for diluting the biocrude feedstock with a diluent (8) which comprises an organic phase which has a viscosity and density lower than that of the biocrude feedstock (1), so as to obtain a dilute biocrude(9)
- a device (b) for contacting (2) the dilute biocrude (9) obtained in dilution device (a) with at least two separate solvents (3,7) including a first solvent (3) which is an aqueous liquid phase with a neutral pH, in particular between 6.5 and 7.5, and a second solvent (7) which is an acidic aqueous liquid phase, having a pH of less than 6.5, said device comprising a column (2) for counter-current liquid-liquid extraction, preferably gravity-based, the first and second solvents having separate inlets and arranged at different heights of the column, in order to obtain, on the one hand, a raffinate (5) comprising the biocrude feedstock depleted in mineral compounds and the diluent, and, on the other hand, an extract (4) comprising, the solvents enriched in mineral compounds
- a device (c) for separating (10) the raffinate obtained with contacting device (b), so as to obtain on the one hand the biocrude feedstock depleted in mineral compounds (11), and, on the other hand, a phase comprising the diluent (8).

16. A facility according to the preceding claim, **characterized in that** at least one of the first and second solvents (3.7) comprises at least two separate inlets arranged at different heights of the column (2).

17. A facility according to one of claims 15 or 16, **characterized in that** at least one of the inputs of the first solvent (3) is at the head of column (2).

18. A facility according to one of claims 15 to 17, **characterized in that** at least one of the inlets of the second solvent (7) is at an intermediate height H_2 of the column (2), in particular at a height H_2 in relation to the total height H of the column such that the ratio H_2/H is between 0.2 and 0.8.

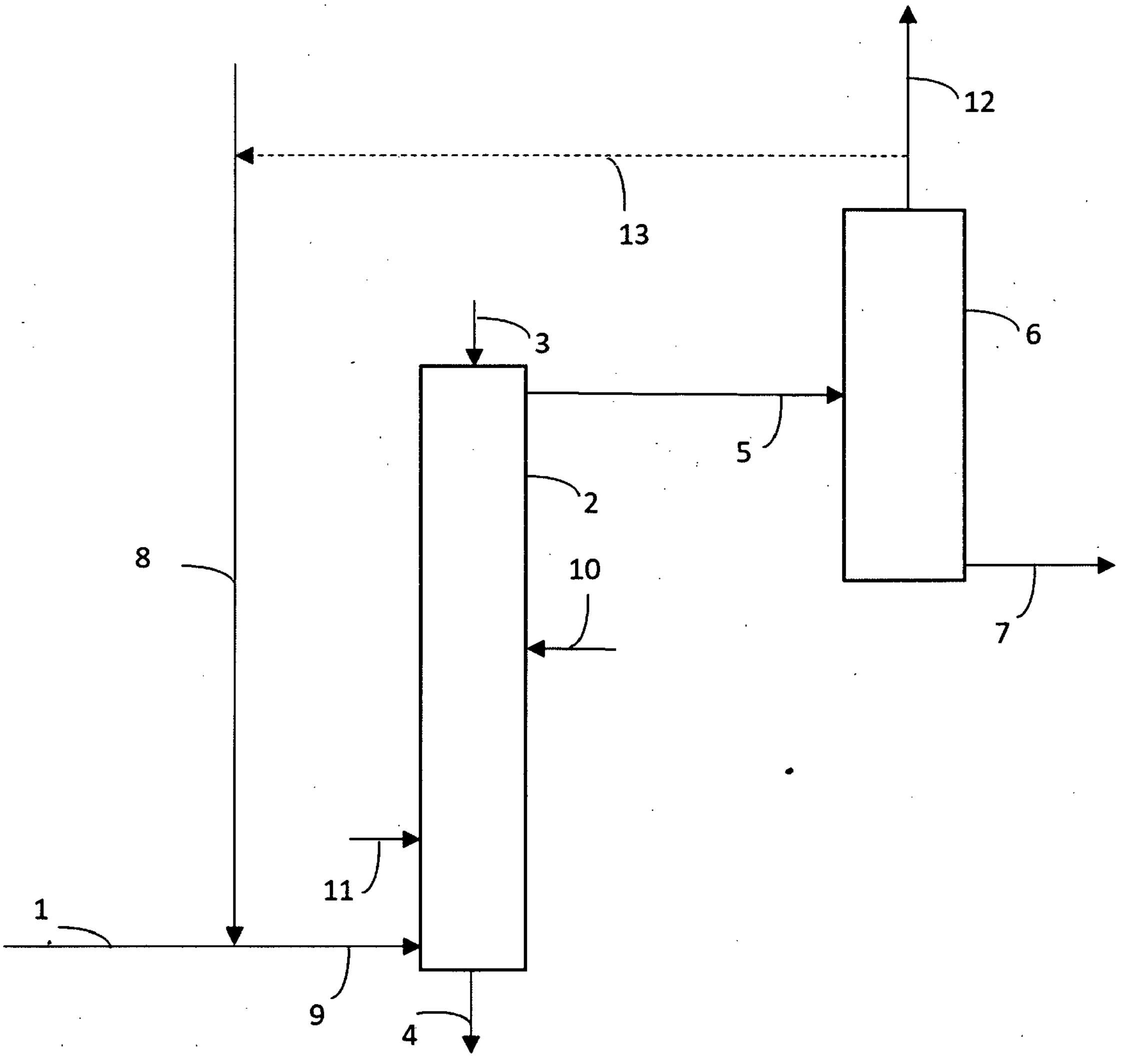
19. A facility according to the preceding claim, **characterized in that** the first solvent has a second inlet (6) in the column at an intermediate height H_3 which is less than the height H_2 of the inlet of the second solvent (7).

20. A facility according to the preceding claim, **characterized in that** the height H_3 of the second inlet (6) of the first solvent is such that, H being the total height of the column, the ratio H_3/H is between 0.05 and 0.4.

21. A facility according to one of claims 15 to 20, **characterized in that** the separation device (10) comprises at least one device selected from a distillation column, an evaporator, an exchanger followed by a separator flask, in particular a so-called "flash" separator flask.

22. A facility according to one of claims 15 to 21, **characterized in that** it comprises a recycling device of at least part of phase (8) comprising the diluent obtained with separation device (c) as a diluent for the diluent for the dilution device (a).

[Fig 1]



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EUROPEAN SEARCH REPORT

Application Number
EP 23 31 5466

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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TECHNICAL FIELDS SEARCHED (IPC)
C10G

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	17 May 2024	Deurinck, Patricia

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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