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(71) Applicant: **VARO Energy Marketing AG**
6340 Baar (CH)

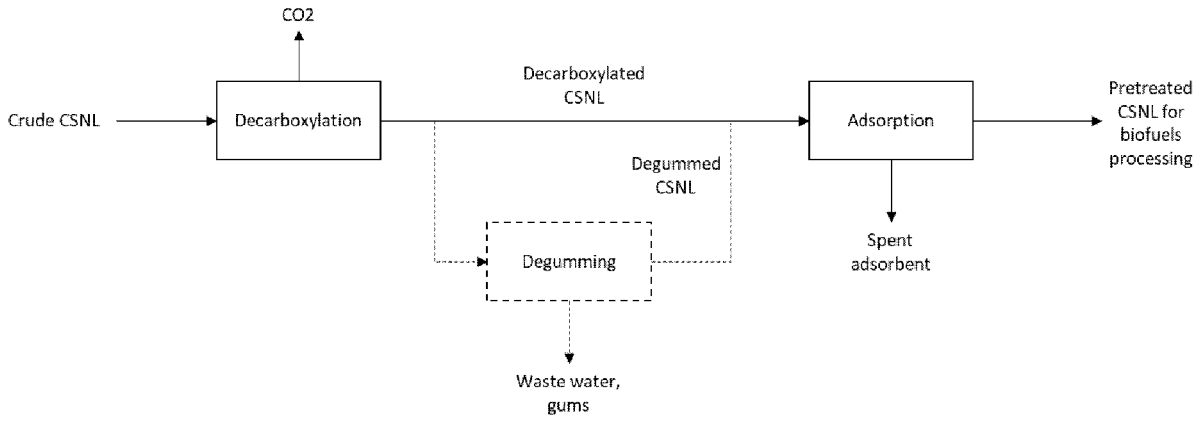
(72) Inventors:
- **Björklöf, Thomas**
  Oberrieden (CH)
- **Weijers, Henk**
  Neuchâtel (CH)

(74) Representative: **Weickert, Jonas**
Thum & Partner
Thum Mötsch Weickert
Patentanwälte PartG mbB
Siebertstraße 6
81675 München (DE)

(54) **CASHEW NUT SHELL LIQUID FOR BIOFUEL APPLICATIONS**

(57) The present invention is directed to a process of treating cashew nut shell liquid comprising the steps of (A) providing a cashew nut shell liquid; (B) heating the cashew nut shell liquid at a temperature in the range of from 120 to 250 °C; (C) contacting the cashew nut shell liquid with at least one adsorbent material and/or at least one filter aid and removing the at least one adsorbent material and/or the at least one filter aid; wherein step (C) is performed after, concurrently with and/or before step (B). The present invention is also directed to a treated cashew nut shell liquid obtainable by the process, as well as a biofuel comprising the treated cashew nut shell liquid. Further, the present invention is directed to the use of the treated cashew nut shell liquid as a biofuel.

Fig. 1



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Description

[0001] The present invention is directed to a process of treating cashew nut shell liquid. The present invention is also directed to a treated cashew nut shell liquid obtainable by the process, as well as a biofuel comprising the treated cashew nut shell liquid. Further, the present invention is directed to the use of the treated cashew nut shell liquid as or in a biofuel.

Background of the Invention

[0002] Most of the world's governments agree by now that global warming poses a serious threat to the future well-being of all people and they agree that it is desirable to reduce the concentration of CO_2 in the atmosphere by lowering the world's emissions of CO_2. This consensus was expressed in part through the Kyoto Protocol (signed in 1997, put into place in 2005), which set targets for emissions reductions by most of the countries of the world.

[0003] Biofuels, i.e., renewable fuels, are regarded as energy sources with the potential to solve a series of problems related to the climate and sustainability. In particular, biofuels are regarded as one of the most viable options for reducing CO_2 emissions in the transport sector. Several governments have set future targets at high market shares of biofuels, and intensively promote programs of increasing the percentage of biofuels relative to fossil fuels.

[0004] Cashew nut shell liquid (CNSL) has potential for use as a biofuel. It may be used either pure or as an additive in fossil fuels. Use of CNSL as biofuel is known in the art, and for example described in US patent application US 2010/0107475 A1. This application discloses a biofuel composition comprising distilled technical cashew nut shell liquid and at least one petroleum product optionally along with plant oils and fuel additive(s).

[0005] Generally, CNSL is extracted from the outer shell of cashew nut obtained from the cashew nut tree, Anacardium Occidentale. CNSL in the shell comprises mainly anacardic acid of different degrees of unsaturation, together with cardol and cardanol. Depending on the extraction method, the content of anacardic acid in the extracted oil may be more than 50 wt.-%.

[0006] Anacardic acid contains more oxygen atoms and has a higher total acid number (TAN) when compared to cardol and cardanol. Oxygen lowers the energy content of CNSL and consumes more hydrogen in the case of fuel processing such as hydroprocessing. All these respective requirements indirectly lead to higher CO_2 emission.

[0007] A further drawback connected with the presence of carboxylic acids is CNSL's corrosivity that limits its direct use as fuel and also leads to material compatibility issues in fuel processing, such as hydroprocessing and others (e.g., hydrodeoxygenation, hydrodewaxing, hydroisomerization, hydrocracking, hydrodearomatization, ring opening reactions, hydrodesulphurization and hydrodenitrogenation etc.).

[0008] Generally, CNSL also contains impurities such as phosphorus, metals and solids. These impurities lower the quality of the produced fuel. As feedstock to hydroprocessing, impurities in CNSL often act as catalyst poison.

[0009] Accordingly, there is a need in the art for further processes of treating CNSL to obtain higher purity grade CNSL for preferred use as biofuels. It is a general desire that production of biofuels is ecologically sustainable why meeting economic standards. The respective issues are desired for new processes of treating CNSL.

Summary of the Invention

[0010] The objective of the present invention is to provide a process that addresses the above-described issues and to provide the respectively treated cashew nut shell liquid (CNSL).

[0011] This object is achieved by a process as defined by claim 1 as well as a product as defined by claim 12. Further aspects of the invention are defined in the dependent claims.

[0012] Accordingly, the present invention provides a process of treating cashew nut shell liquid comprising the steps of:

(A) providing a cashew nut shell liquid;
(B) heating the cashew nut shell liquid at a temperature in the range of from 120 to 250 °C; and
(C) contacting the cashew nut shell liquid with at least one adsorbent material and/or at least one filter aid and removing the at least one adsorbent material and/or the at least one filter aid;

wherein step (C) is performed after, concurrently with and/or before step (B).

[0013] The present invention also provides a treated cashew nut shell liquid obtainable by the process, as well as a biofuel comprising the treated cashew nut shell liquid and use of the treated cashew nut shell liquid as or in a biofuel.

[0014] The present invention allows for lowering the content of carboxylic acids, the general oxygen content as well as the contents of further impurities in CNSL, which may adversely affect further processing of CNSL to biofuel or its use as biofuel.

[0015] For the process according to the present invention, already present and established refinery equipment may be used. For example, reactors used in oil refinery and/or fossil fuel processing may be employed. This allows meeting aspects of sustainability and economy. Further, several steps of the process may be carried out by relatively low temperatures, thus lowering energy consumption.

Short Description of the Figures

[0016]

Figure 1 illustrates one embodiment of the process according to the present invention, where the decarboxylation step precedes the adsorption step.

Figure 2 illustrates another embodiment of the process according to the present invention, where the adsorption step precedes the decarboxylation step.

Detailed Description of the Invention

[0017] The present invention provides a process of treating cashew nut shell liquid (CNSL).

[0018] Throughout this disclosure, the wording "cashew nut shell liquid" or "CNSL" is used to describe both the cashew nut shell liquid (CNSL) used as a starting material for the present treatment process as well as the cashew nut shell liquid (CNSL) respectively treated in any of the steps of the treatment process. Accordingly, this wording does not describe any structural component but rather the origin of the obtained product, i.e., being CNSL. For examples, cashew nut shell liquid (CNSL) may identify the natural or technical CNSL used as a starting material. Cashew nut shell liquid (CNSL) may also identify the product obtained after any one, some or all of steps A, B, C and D. It may also identify the product obtained after hydroprocessing. As is obvious, after some of the steps of the treatment process, the CNSL does not contain its original chemical structure. The CNSL product obtained by the process according to the invention is also identified herein as "treated CNSL".

Cashew nut shell liquid (CNSL)

[0019] In step (A) of the process according to the present invention, a cashew nut shell liquid (CNSL) is provided.

[0020] Cashew nut shell liquid (CNSL) occurs as a brown viscous liquid in the soft honeycomb structure of the shell of cashew nut, a plantation product obtained from the cashew tree, *Anacardium Occidentale.* Native to Brazil, the tree grows in the coastal areas of Asia and Africa.

[0021] Cashew nut attached to cashew apple is grey colored and kidney shaped. The shell is about 0.3 to 0.4 cm thick, having a soft leathery outer skin and a thin hard inner skin. Between these skins, a honeycomb structure containing the phenolic material popularly called "cashew nut shell liquid" (CNSL) is located. The kernel is inside the shell wrapped in a thin brown skin, known as the testa.

[0022] Usually, the nut consists of the kernel (about 20 to 25 wt.-%), the shell liquid (about 20 to 35 wt.-%) and the testa (about 2 wt.-%), the rest being the shell.

[0023] According to the invention, the CNSL in step (A) may be provided in any possible way by any separation method known in the art. It may be purchased from many suppliers under the CAS No. 8007-24-7.

[0024] CNSL is traditionally obtained as a by-product during the process of removing the cashew kernel from the nut. CNSL may be removed from the nut shells by extractions methods that can be classified into two basic types: those that involve heating and those that are performed in cold or room temperature. CNSL obtained in the cold is denoted as natural CNSL and that extracted by a hot method is called technical CNSL. Natural CNSL usually contains anacardic acid (e.g., about 70 to 80 wt.-%), cardol (e.g., about 10 to15 wt.-%), and minor quantities of 2-methyl cardol, cardanol and polymeric material, while technical CNSL usually contains cardanol (e.g., about 50 to 65 wt.-%), cardol (e.g., about 10 to 12 wt.-%), methyl cardol (e.g., about 1 to 2 wt.-%) and polymeric material (e.g., about 10-30 wt.-%). Although CNSL is considered a vegetable oil, it is not a triglyceride oil.

[0025] In the cold extraction method, CNSL can be obtained by extraction with a solvent or by a squeezing method.

[0026] For squeezing extraction, cashew nut shells are usually cut or crushed into pieces to maximize their attainment through pressing at room temperature, followed by filtration. An oil expeller/oil press comprising rotating screws may be used for crushing and applying pressure on the shells to squeeze CNSL.

[0027] Cold solvent extraction uses solvents such as hexane, acetone, diethyl ether or light petroleum (e.g., at 40 to 60 °C). For example, cashew nut shells are crushed and submerged in hexane at room temperature. Afterwards, the shells are removed (e.g., by filtration) and the solvent may be evaporated at lower temperatures (e.g., about 50 °C - depending on the solvent used).

[0028] Extraction methods such as Soxhlet solvent extraction or ultrasound solvent extraction are also possible cold extraction techniques.

[0029] The advantage of a cold extraction method is that these methods are less energy consuming and more sustainable due to the cold temperatures used. They provide natural CNSL that is heated in a further step to reach decarboxylation. Since the amount of the natural CNSL is lower when compared to the entire cashew nut shells, less energy is consumed to reach the required decarboxylation temperature, leading to further energy saving.

[0030] Heat extraction methods used are, in particular, roasting or hot oil methods.

[0031] The roasting method can be achieved by heating cashew nut shells in open pans or drums at high temperatures e.g., in the range of from 400 to 700 °C. Mostly, this technique is used in conjunction with an oil expeller to yield an extent of up to 90 wt.- % of total CNSL in the shell.

[0032] In a thermomechanical (hot oil) method, cashew nut shells can be heated by the actual CNSL. For example, a so-called "hot oil bath process" may be used,

in which raw cashew nut shells are heated at e.g., 180 to 200 °C whilst held on a slowly traveling conveyor belt submerged into CNSL bath. During the heating process, anacardic acid present in the shells gets decarboxylated to cardanol. Thus, an advantage of heat extraction is the concurrent decarboxylation of CNSL in the same step.

[0033] The above-described extraction methods may also be combined for more efficient extraction of CNSL from the cashew nut shells.

[0034] Technical CNSL may further be processed by distillation at reduced pressure to efficiently remove high contents of the polymeric material (often present in the range of from 10 to 30 wt.-%). The composition of distilled technical CNSL usually contains approximately 75 to 80 wt.-% cardanol, 5 to 10 wt.-% cardol and less than 5 wt.-% polymeric material. However, a distillation step is not necessarily required to be used in the process according to the present invention, for example if reduction of energy consumption is an issue. In some embodiments, polymeric material is removed by filtration and/or centrifugation.

[0035] Step (A) of the process according to the present invention may either be carried out before or concurrently to step (B).

[0036] For example, if natural CNSL is provided, the heating step (B) is carried out after step (A).

[0037] In order to provide technical CNSL, extraction and decarboxylation by heating, and, thus, steps (A) and (B) of the process, are carried out concurrently. However, an additional heating step (B) may also be applied to reach more efficient decarboxylation.

[0038] The process according to the present invention is particularly suitable for the treatment of natural CNSL, i.e., as obtained by a cold extraction method. However, the process may also be used to treat technical CNSL and improve its quality.

Heating / Decarboxylation

[0039] The extracted CNSL is subjected to a heating step for removal of CO_2 from anacardic acid (decarboxylation, step (B)).

[0040] Step (B) of the process according to the present invention requires heating the cashew nut shell liquid (CNSL) at a temperature in the range of from 120 to 250 °C, preferably from 130 to 220 °C, more preferably from 140 to 200 °C. The heating may be performed at a temperature of at least 120 °C, preferably at least 130 °C, and more preferably at least 140 °C and/or at a temperature of up to 250 °C, preferably up to 220 °C, and more preferably up to 200 °C.

[0041] Preferably, step (B) is performed for a time period of from 30 minutes to 2 hours, more preferably from 45 to 90 minutes, and most preferably from 50 to 70 minutes. Step (B) may be performed for at least 30 minutes, preferably for at least 45 minutes, and more preferably for at least 50 minutes and/or for up to 2 hours, preferably for up to 90 minutes, and more preferably for up to 70 minutes. In some embodiments, the heating is performed at atmospheric pressure.

[0042] If step (B) is prepared by the aid of a column reactor (e.g., a deodorization column), much shorter time periods may be used (e.g., 5 to 30 minutes).

[0043] Step (B) leads to decomposition of the anacardic acid in CNSL into cardanol and carbon dioxide (CO_2). Thus, decarboxylation of CNSL involves loss of a carbon dioxide molecule from anacardic acid, and conversion of anacardic acid to cardanol. The generated carbon dioxide is removed from the CNSL. It may escape freely from the device and/or may actively be removed by e.g., applying a negative pressure.

[0044] Generally, oxygen lowers the energy content of CNSL and consumes more hydrogen in the case of fuel processing such as hydroprocessing. Carboxylic acids in CNSL make it more sensitive to corrosivity. This limits its direct use as fuel and also leads to material compatibility issues in fuel processing, such as hydroprocessing and others (e.g., hydrodeoxygenation, hydrodewaxing, hydroisomerization, hydrocracking, hydrodearomatization, ring opening reactions, hydrodesulphurization and hydrodenitrogenation, etc.). These drawbacks are eliminated or at least decreased by applying step (B).

[0045] Step (B) may be performed in any kind of vessel (e.g., an open vessel), as long the generated carbon dioxide has a chance to escape and/or to be removed by a gas outlet. Step (B) may also be performed during any hot CNSL extraction method as described above for step (A) (e.g., as a roasting or hot oil extraction process).

[0046] Step (B) may be performed in the presence or absence of a catalyst. Preferred catalytic substances include alkali and alkaline earth metal (preferably, magnesium) such as oxides and hydroxides thereof, which are added in an amount of from 0.5 to 5 wt.-% based on the CNSL weight. Use of a catalyst in the process according to the present invention reduces the temperature required for the decarboxylation reaction. For example, temperatures in the range of from 125 to 150 °C may be effective in decarboxylation in the presence of a catalyst, while without a catalyst, higher temperatures, e.g., in the range of from 170 to 200 °C could rather be required for efficient decarboxylation. Preferably, step (B) is performed in the absence of a catalyst. It has the advantage that no extra process step is required for removal of the catalyst.

[0047] Preferably, step (B) leads to preparation of a CNSL having a total acid number (TAN) of less than 10 mg KOH/g, preferably less than 5 mg KOH/g, determined according to ASTM D 664.

[0048] The total acid number is a measurement of the acidity of an oil which is determined by the number of milligrams of potassium hydroxide (KOH) needed to neutralize acids in one gram of oil.

[0049] Step (B) reduces the number of acids by decarboxylation of anacardic acid to cardanol. Accordingly, step (B) decreases the total acid number of the CNSL.

Adsorption and/or filtering

[0050] The CNSL is subjected to an adsorption and/or filtering step for removal of impurities and decolorization (step (C)).

[0051] In step (C) of the process according to the present invention, the cashew nut shell liquid (CNSL) is contacted with at least one adsorbent material and/or at least one filter aid, and the at least one adsorbent material and/or at least one filter aid are then removed from the CNSL.

[0052] Step (C) intends to remove or at least decrease the number of impurities present in CNSL. Such impurities may comprise general solids, phosphorus, metals and other coloring pigments and compounds that may otherwise impart the preparation of CNSL to biofuel or its use as or in a biofuel. For example, impurities in CNSL may act as catalyst poison during hydroprocessing reactions or cause fouling during use as fuel in an engine.

[0053] in some embodiments, the contacting in step (C) is carried out for a time period of from 1 to 60 minutes, more preferably from 15 to 45 minutes; and the time period is, in particular dependent, on the adsorption/filtering technique and/or the kind of material used.

[0054] The temperature is similarly dependent on the adsorption and/or filtering technique, and/or the kind of material used. In some embodiments, the temperature is in the range of from 20 to 120 °C, more preferably from 30 to 110 °C.

[0055] Preferably, the at least one adsorbent material and/or the at least one filter aid is selected from the group consisting of clay such as e.g., bentonite clay, silica, activated carbon, diatomaceous earth, and cellulose-based filter aids. Another example of clay is Fuller's earth. As filter aids, paper or membrane (e.g., cellulose-membrane) filters may be used. Commercially used pressure leaf filters or filter press or similar may be employed in this step.

[0056] In some embodiments, the filter aid has a pore diameter in the range of from 0.1 to 100 μm, which can be determined e.g., by Capillary Flow Porometry (CFP) according to standard protocols.

[0057] In some embodiments, the adsorbent material comprises particles, the particles preferably having a diameter (D50) in the range of from 0.1 μm to 2 mm, more preferably from 1 to 50 μm, measured by microscopy methods (e.g., scanning electron microscopy (SEM)) or sieve techniques.

[0058] Concentration of the at least one adsorbent material and/or the at least one filter aid is preferably in the range of from 0.1 to 20 wt.-%, more preferably from 0.3 to 10 wt.- %, and most preferably from 0.5 to 5 wt.-%, based on the weight of CNSL.

[0059] In step (C), one adsorbent material and/or one filter aid, or two or more adsorbent materials and/or two or more filter aids may be used. In the case that more than one adsorbent material and/or filter aid are used, they may be contacted with CNSL concurrently and/or sequentially.

[0060] In some embodiments, CNSL is filtered by a filter aid and subsequently or concurrently contacted with an adsorbent material. The dimensions of the pore diameter may be chosen based on the particle size of the adsorbent material. A different order, i.e., first contacting with adsorbent material and then filtration is also possible.

[0061] In some embodiments, CNSL is passed directly through a cellulose-based membrane filter, wherein the contact time is very short (e.g., several seconds such as from 1 to 10 seconds).

[0062] For example, CNSL may be contacted with 0.5 to 5 wt.-% of an adsorbent material (e.g., a clay having a particle size (D50) in the range of from 1 to 20 μm) in a reactor, preferably a stirring reactor, at a temperature in the range of from 30 to 110 °C. The contacting process is carried out for 15 to 45 minutes, preferably by constant stirring. After the contacting time, the mixture is passed through a pressure leaf filter, a filter press or similar (preferred pore diameter being in the range of from 0.2 to 40 μm) to remove the adsorbent material and other solids from the CNSL. Purification degree of CNSL may be analyzed, if required, by any suitable method, for example by ICP-MS or ICP-OES spectrometry.

[0063] The sequence of steps (B) and (C) may be interchangeable. Step (C) may be performed after, concurrently with and/or before step (B).

[0064] In some embodiments, step (C) is performed before step (B). Employing the process steps in this order, solid particles could be removed by step (C) which could prevent fouling of the equipment used for step (B).

[0065] In some embodiments, step (C) is performed after step (B). By such an order of steps, it may be avoided that anacardic acid reacts with the adsorbent material and/or filter aid and is removed from CNSL. As step (B) decreases the total acid number (TAN) of the CNSL, the materials (i.e., reactor materials) used in step (C) require a lower acid and corrosion resistance.

[0066] In some embodiments, step (C) is performed concurrently with step (B). For example, CNSL may be contacted with the at least one adsorbent material and/or at least one filter aid at a higher temperature that is sufficient to decarboxylate CNSL.

[0067] In the process according to the present invention, steps (B) and/or (C) may be repeated, if required, with similar or different embodiments of each of the steps.

Degumming

[0068] The CNSL may be subjected to an optional degumming step to remove further undesired components (step (D)).

[0069] The process according to the present invention may comprise an optional step (D) comprising adding water and optionally at least one acid to the cashew nut shell liquid, mixing the components and removing the water and optional at least one acid.

[0070] Generally, degumming is a process for removal of phosphatides (i.e. phospholipids) from vegetable oils. Phosphatides are also called gums (e.g., lecithin is the common name for phosphatidyl choline). They tend to foam formation upon heating, and adversely affecting the use of CNSL in several applications. Degumming may also be used for preparing CNSL for long-term storage or transport. In the present process, the degumming step is a further purification step. Different components or impurities of CNSL such as e.g., proteinaceous and mucilaginous materials and metals may be removed by this step.

[0071] Step (D) describes both water and acid degumming processes. Accordingly, either water degumming (for removal of rather hydratable components) or acid degumming (for removal of less hydratable components) or both processes may be performed by step (D).

[0072] The degumming process may be a simple washing step to remove impurities, comprising adding water and optionally at least one acid to the cashew nut shell liquid, mixing the components and removing the water and optional at least one acid.

[0073] For example, in the water degumming process of step (D), water (preferably at a temperature in the range of from 20 to 100 °C) is added to CNSL and mixed, preferably for a time period of from 15 to 60 minutes, more preferably from 20 to 40 minutes. Preferably, water and CNSL are both warm (e.g., in the range of from 30 to 100 °C) in order to promote flow and bonding (i.e., to lower viscosity). The water molecules bond with the hydratable impurities to create a larger mass of material. This material is then removed, e.g., via filtration, decanting after settling and/or centrifugation (e.g., by a vertical disk-stack centrifuge). The amount of water used will vary depending on the amount of impurities present in CNSL. Preferably, a water excess (by weigh) over the expected impurities content of from 2 to 10 is used. If this content is not known, a content of 5 wt.-% impurities of CNSL is assumed. After the degumming process, remaining water may be removed from CNSL by drying (e.g., vacuum drying).

[0074] For example, in the acid degumming process of step (D), water and at least one acid are added to CNSL and the mixture is treated as described for the water degumming process. The addition of water and acid may be carried out concurrently or sequentially. The adjusted pH is preferably between pH 2 and 5. The at least one acid is preferably selected from the group consisting of citric, phosphoric and sulphuric acid. Before separation, the pH may also be adjusted to a higher pH by the addition of a base, preferably selected from NaOH or KOH.

[0075] Preferably, step (D) is performed before step (C). The advantage of such an order of steps is that lower amounts of adsorbent material can be used in step (C) as several impurities (e.g., metals) are already removed in step (D). Step (C) preferably removes an amount of the remaining phosphatides.

[0076] Preferably, step (D) is also carried out before step (B), as it may be advantageous to remove high amounts of phosphatides or other impurities before heating CNSL.

[0077] In a preferred embodiment, step (D) is carried out before step (C) and step (B). This order of steps would enable using existing processing plants, such as vegetable oil refining plants, for the process according to the invention. In this scenario, a deodorization column could be used as heat treatment reactor in step (B), and may be possibly run at a slightly lower temperature than deodorizing of vegetable oils (usually about 250 °C).

[0078] In one embodiment, the process according to the present invention comprises the order of steps: step (A) - step (B) - (optionally: step (D)) - step (C).

[0079] In another embodiment, the process according to the present invention comprises the order of steps: step (A) - (optionally: step (D)) - step (C) - step (B).

[0080] In still another embodiment, the process according to the present invention comprises the order of steps: step (A) - (optionally: step (D)) - step (B) - step (C).

Further process steps

[0081] The process according to the present invention may comprise further steps.

[0082] In some embodiments, any of the steps (B), (C) and/or (D) may be repeated with similar or different embodiments.

[0083] Preferably, the process according to the present invention further comprises one or more steps that are known from fossil fuel or vegetable oil processing.

[0084] In some embodiments, the process according to the present invention further comprises one or more steps that are used to lower the boiling point and/or decrease viscosity of CNSL and/or to further purify CNSL.

[0085] The process according to the present invention may further comprise at least one step selected from the group consisting of neutralization, hydroprocessing such as hydrodeoxygenation, hydrodewaxing, hydroisomerization, hydrodearomatization, ring opening reactions, hydrodeoxygenation, hydrodesulphurization, hydrodenitrogenation, fluid catalytic cracking and hydrocracking of the cashew nut shell liquid (CNSL).

[0086] Preferably, the further step(s) is/are carried out after steps (A) - (D) of the process. However, in some embodiments, further step(s) may be carried out before any one of steps (B), (C) or (D).

[0087] In some embodiments, a neutralization step is further included, wherein - preferably after step (D) - an alkali solution, preferably containing NaOH or KOH, is added to CNSL in order to adjust the pH to a higher value, preferably a pH of 6 to 8, more preferably 6.5 to 7.5. The mixture is preferably agitated at an enhanced temperature (preferably in the range of from 50 to 70 °C, 10 to 60 minutes) and the alkali solution is separated, preferably by decanting or centrifugation. The main purpose of

neutralization is to neutralize and remove the free fatty acids if present in CNSL and to remove acidity in CNSL. Other impurities such as metals, color pigments etc. may also be removed by this step.

[0088] In some embodiments, at least one hydroprocessing step such as e.g., hydrodeoxygenation, hydrodewaxing, hydroisomerization, hydrocracking, hydrodearomatization, ring opening reactions, hydrodesulphurization and/or hydrodenitrogenation, is included. For example, the process may comprise two, three or more of these hydroprocessing steps.

[0089] Hydroprocessing is a method that uses high pressure hydrogen to remove contaminates from CNSL. For example, contaminants comprising oxygen, sulphur and/or nitrogen are hydrated and removed from CNSL. Usually, CNSL tends to contain very low or no contents of sulphur. Further, the hydroprocessing step may lead to saturation of double bonds in olefins and aromatics, cracking and ring opening reactions.

[0090] For example, the CNSL may be subjected to a catalytic hydroprocessing step carried out in the presence of hydrogen, to yield an effluent, which may be subjected to fractionation and/or further processing steps for providing liquid fuels and other chemicals. Also, gasoline fractions may be produced that can be used as a bio-naphtha component or as raw material for bio-plastics.

[0091] As described in US 11,053,452 B2, hydroprocessing may be performed using one or more hydroprocessing catalysts comprising one or more metals selected from Group VIA and Group VIII metals (Periodic Table of Elements). Particularly useful examples are Mo, W, Co, Ni, Pt and Pd. The catalyst(s) can also contain one or more support materials, for example zeolite, alumina (Al_2O_3), gamma-alumina, zeolite-alumina, alumina-silica (SiO_2), ZrO_2, alumina-silica-zeolite and activated carbon. Suitably a mixture of CoO and MoO_3 (CoMo) and/or a mixture of NiO and MoO_3 (NiMo), and/or a mixture of Ni, Mo and Co and/or NiW and one or more support materials selected from zeolite, alumina, silica, zeolite-alumina, alumina-silica, alumina-silica-zeolite and activated carbon. Also, noble metals, such as Pt and/or Pd dispersed on gamma-alumina may be used.

[0092] Hydroprocessing may be carried out under a pressure of 5 to 300 bar (total pressure, abs). In some embodiments, the pressure in the hydroprocessing is from 30 to 250 bar, preferably from 30 to 120 bar.

[0093] The hydrogen partial pressure may be maintained in the range of from 50 to 250 bar, preferably from 80 to 200 bar, particularly preferably from 80 to 110 bar.

[0094] Hydroprocessing may be carried out at a temperature in the range of from 100 to 450° C, preferably from 280° C to 450° C., more preferably from 350° C to 400° C.

[0095] Hydroprocessing feed rate WHSV (weight hourly spatial velocity) of the CNSL feed is proportional to an amount of the catalyst. The WHSV of the feed material preferably varies between 0.1 and 10, it is suitably in the range of from 0.1 to 5 and more preferably from 0.3 to 0.7.

[0096] The ratio of H2/feed may vary between 600 and 4000 Nl/l, suitably of 1300-2200 Nl/l.

[0097] The CNSL feed is pumped to the hydroprocessing reactor at a desired speed. Suitably the feed rate LHSV (liquid hourly space velocity) of the feed material is in the range of from 0.01 to 10 h^{-1}, preferably 0.1 to 5 h^{-1}.

[0098] Preferably, the liquid hydrocarbon stream obtained after the hydroprocessing step(s) on CNSL includes fuel grade hydrocarbons having a boiling point of at most 380° C according to ISO EN 3405. The person skilled in the art is able to vary the distilling conditions and to change the temperature cut point as desired to obtain any suitable hydrocarbon product, preferably having suitable boiling conditions in the transportation fuel ranges.

[0099] In some embodiments, the hydroprocessing step is a hydrocracking step. Hydrocracking converts high-boiling constituents of CNSL to low-boiling constituents by hydrogen treatment, and thus lowers the boiling point of CNSL. Alternatively, fluid catalytic cracking may be used. For example, cracking of CNSL with a molecular sieve at a temperature in the range of from 400 to 600 °C for a time period in the range of from 1 to 2 hours is applied.

[0100] In the process according to the present invention, any of the above-described steps of the different embodiments may be carried out in addition to the steps (A) to (D) of the process. The process according to the present invention may comprise only one additional step or two or more of these additional steps. The process of the present invention may comprise only steps (A) to (C) and optionally (D).

Product and use

[0101] The present invention also provides a treated cashew nut shell liquid (CNSL) obtainable and/or obtained by the process according to any one of the embodiments of the process.

[0102] The CNSL treated by the process according to the present invention ("treated CNSL" in the following) is characterized by a high content of cardanol, and respectively low content of anacardic acid and low total acid number (TAN). Further, it preferably has low contents of impurities and also low viscosity.

[0103] Based on its advantageous characteristics and the purity grade, the treated CNSL may be used in a variety of applications. For example, it may be used in polymer-based industries such as friction linings, paints and varnishes, laminating resins, rubber compounding resins, cashew cements, polyurethane-based polymers, surfactants, epoxy resins, foundry chemicals and intermediates for chemical industry. In these industries it may replace the hitherto used fossil-based materials.

[0104] Preferably, the treated CNSL is used in biofuel applications. Accordingly, the present invention also provides a biofuel comprising the treated cashew nut shell liquid (CNSL) obtainable and/or obtained by the process

according to any one of the embodiments of the process.

[0105] Further, the present invention provides use of the treated cashew nut shell liquid (CNSL) obtainable and/or obtained by the process according to any one of the embodiments of the process, as a biofuel.

[0106] In the sense of the present invention, "biofuel" is considered any fuel produced from biomass, i.e., biological material derived from living, or recently lived, organisms. Hence, biofuel is considered any hydrocarbon fuel that is produced from organic matter living or once living material in a short period of time (days, weeks, or even months), such as plants, animals, and microorganisms.

[0107] In the sense of the present invention, any fuel is also considered as a "biofuel" if it comprises a fuel produced from biomass. Thus, any fuel product comprising the treated CNSL is considered a biofuel.

[0108] The treated CNSL may be contained in any amount in a fuel product. It may be the single fuel component of the fuel product or may be a blend with other components, such as e.g., other biofuels or conventional fuels. In some embodiments, the treated CNSL is contained in a fuel product in an amount of from 1 to 50 wt.-%, more preferably from 2 to 25 wt.-%.

[0109] The biofuel or fuel product may comprise additives commonly used in this field, such as, e.g., stabilizers, lubricants or combustion additives.

[0110] Generally, several properties are to be considered as important for the selection of biofuel such as viscosity, flash point, fire point, cloud point, pour point, density, calorific value, corrosive nature, miscibility, sulphur content, molecular weight, cetane number, etc. In the treated CNSL, many of the properties are in the similar range as in conventional fuels. Thus, the treated CNSL is well suited as a replacement for conventional fuels or in blends or mixtures with conventional fuels, in particular, marine fuels.

[0111] The treated CNSL may be used directly as biofuel (e.g., after the steps (A) to (D)) or it may undergo further process steps. For example, after one or more hydroprocessing steps, pure hydrocarbon biofuel, preferably renewable diesel, is prepared. The hydroprocessed CNSL is suitable in or as transportation diesel, e.g., road diesel or aviation fuel.

[0112] The treated CNSL may be used in blends or mixtures with conventional fossil fuels, or may be used as additive therein. Different blends of the treated CNSL will have different properties and application. For example, use of the treated CNSL as an additive in engines may increase the durability of the equipment. Application of the treated CNSL as a bioadditive may reduce the dependency on petroleum products besides preserving the environment by lowering pollutant residues from fuel combustion products.

[0113] The treated CNSL may be used as an alternative fuel for diesel engine. For example, it may be used in the compression ignition engine in blend with conventional diesel.

[0114] A biofuel comprising the treated CNSL is considered as offering many advantages, including sustainability, decrease of HC, CO, NOx gas emissions and many other harmful pollutants.

[0115] The below examples shall serve to further illustrate specific embodiments of the present invention.

Examples

Example 1

[0116] Natural cashew nut shell liquid (CNSL, about 1 kg) was used. Generally, CNSL may be extracted from cashew nut shells using an extraction plant comprising an oil expeller/oil press. By this device, rotating screws push cashew nut shells through a chamber. Compression on the shells is reached by the screw rotation, and CNSL is squeezed out from the shells and expelled out through the gaps in the chamber. In this way, CNSL is separated from the shells.

[0117] CNSL is filtered through a filter paper in order to remove coarse particles, and is collected in a batch reactor. The reactor is heated to a temperature of 50 °C under constant stirring at 500 rpm. 200 ml of water (at a temperature of about 60°C) are added and pH of was adjusted to about pH 3 by addition of phosphoric acid and stirring is continued for 30 min at 50 °C. The mixture is transferred to a centrifuge vessel and centrifugation is carried out at 2,000 rpm for 5 min. The water-acid phase is decanted for removal. Vacuum drying is performed in order to remove remaining water from CNSL. CNSL is again placed in a stirring reactor and heated to 50 °C. 20 g of Tonsil® (by Clariant) is added and agitation at 200 rpm is carried out at 90 °C for 30 min. The mixture is filtered (11 μm pore size filter) to remove the adsorbent. The filtrate is passed through a deodorization column at a temperature of 180 °C to remove carbon dioxide. The obtained CNSL (about 600 g) is separated into 3 portions (Samples 1 to 3) for further treatment. Sample 1 remains unchanged.

Example 2

[0118] Hydroprocessing is performed on Sample 2.

Example 3

[0119] Catalytic cracking (molecular sieve, 500 °C) is performed on Sample 3.

[0120] The samples are analyzed for their contents by GCMS and FTIR.

Claims

1. A process of treating cashew nut shell liquid comprising the steps of:

(A) providing a cashew nut shell liquid;
(B) heating the cashew nut shell liquid at a temperature in the range of from 120 to 250 °C;
(C) contacting the cashew nut shell liquid with at least one adsorbent material and/or at least one filter aid and removing the at least one adsorbent material and/or the at least one filter aid;

wherein step (C) is performed after, concurrently with and/or before step (B).

2. The process according to claim 1,
further comprising a step (D) of adding water and optionally at least one acid to the cashew nut shell liquid, mixing the components and removing the water and optional at least one acid, wherein step (D) is preferably performed before step (C).

3. The process according any one of the preceding claims, comprising the order of steps of:
step (A) - step (B) - optionally: step (D) -step (C).

4. The process according to any one of claims 1 or 2, comprising the order of steps of:
step (A) - optionally: step (D) - step (C) - step (B).

5. The process according to any one of claims 1 or 2, comprising the order of steps of:
step (A) - optionally: step (D) - step (B) - step (C).

6. The process according to any one of claims 2 to 5, wherein in step (D), the pH is adjusted by the addition of a base, preferably selected from NaOH or KOH.

7. The process according to any one of claims 2 to 6, wherein the acid in step (D) is selected from the group consisting of citric, phosphoric and sulphuric acid.

8. The process according to any one of the preceding claims,
wherein after step (B), the total acid number of the cashew nut shell liquid is less than 10 mg KOH/g, preferably less than 5 mg KOH/g, determined according to ASTM D 664.

9. The process according to any one of the preceding claims,
wherein step (B) is performed for a time period of from 30 minutes to 2 hours, preferably from 45 to 90 minutes.

10. The process according to any one of the preceding claims,
wherein the at least one adsorbent material and/or the at least one filter aid is selected from the group consisting of clay such as bentonite clay, silica, activated carbon, diatomaceous earth, and cellulose-based filter aids.

11. The process according to any one of the preceding claims,
further comprising at least one step selected from the group consisting of neutralization, hydrodeoxygenation, hydrodewaxing, hydroisomerization, hydrocracking, hydrodearomatization, ring opening reactions, hydrodeoxygenation, hydrodesulphurization, hydrodenitrogenation, and fluid catalytic cracking.

12. A treated cashew nut shell liquid obtainable by the process according to any one of the preceding claims.

13. A biofuel comprising the treated cashew nut shell liquid according to claim 12.

14. Use of the treated cashew nut shell liquid according to claim 12 as a biofuel.

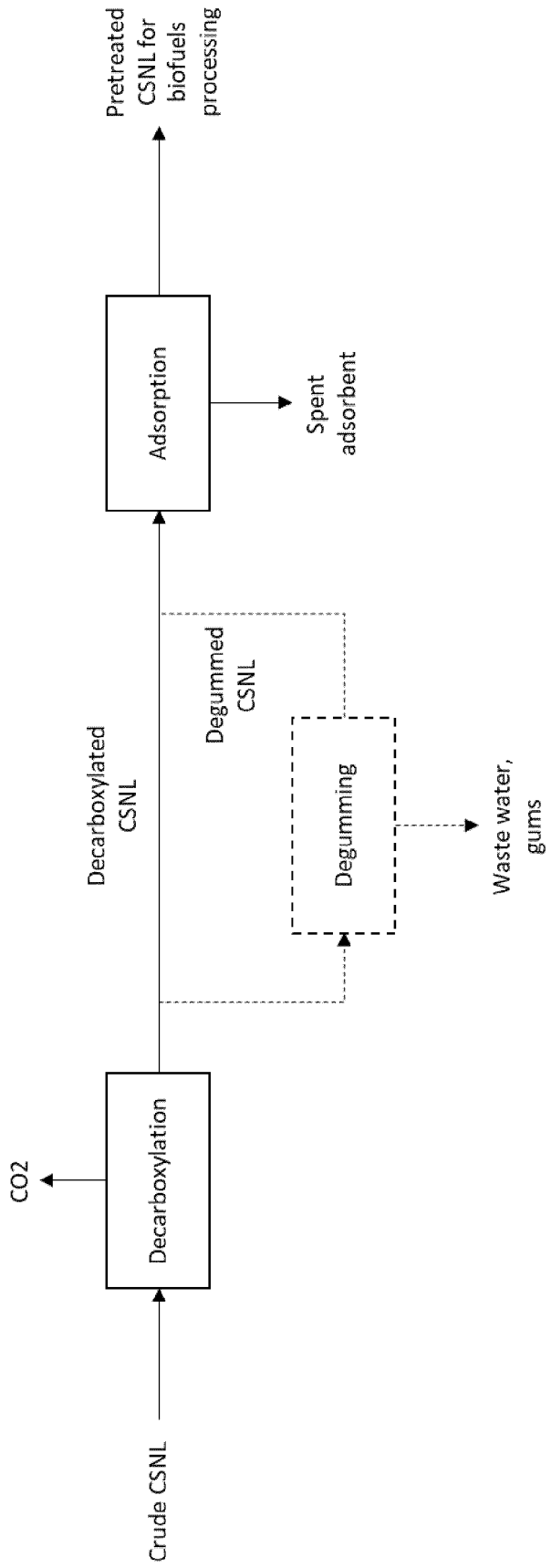
Pretreated CSNL for biofuels processing
Adsorption
Spent adsorbent
Degummed CSNL
Decarboxylated CSNL
Degumming
Waste water, gums
CO2
Decarboxylation
Crude CSNL

Fig. 1

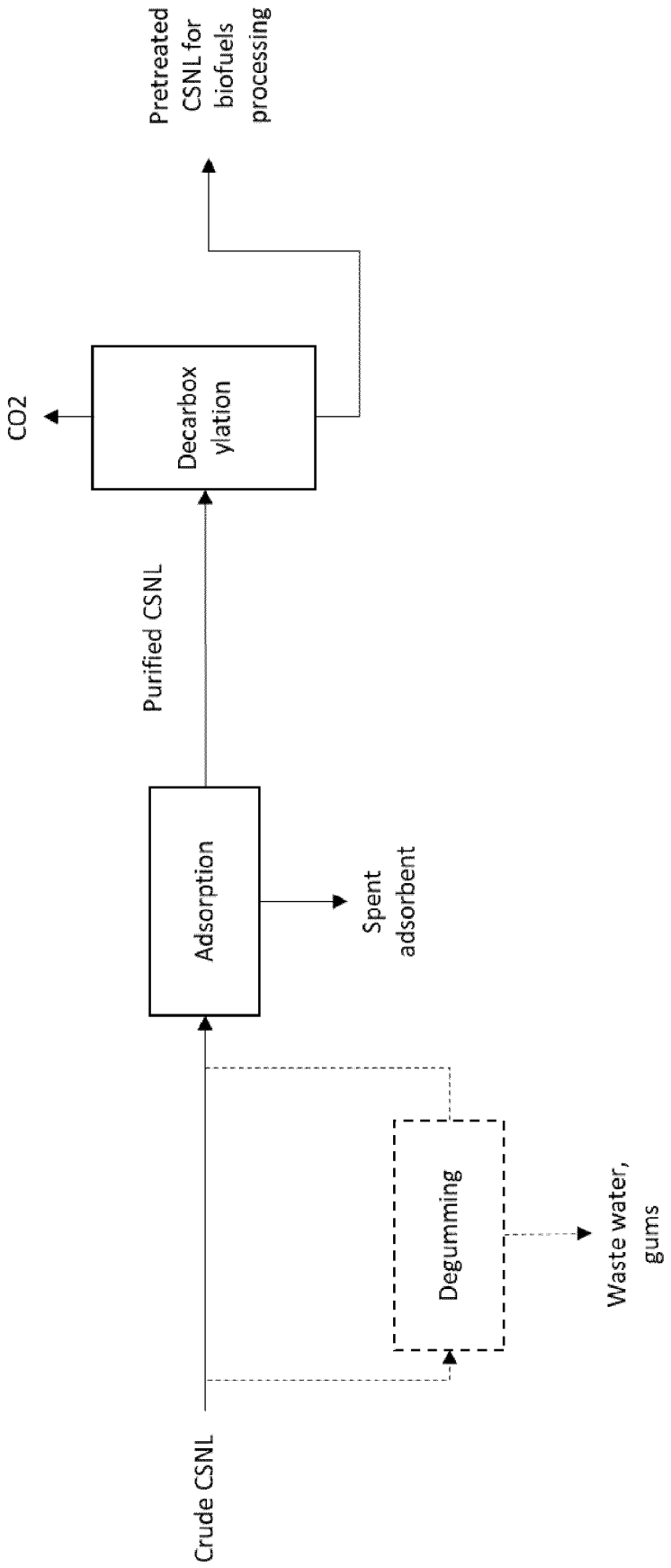
Pretreated CSNL for biofuels processing
CO2
Decarbox ylation
Purified CSNL
Adsorption
Spent adsorbent
Degumming
Waste water, gums
Crude CSNL

Fig. 2

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EUROPEAN SEARCH REPORT

Application Number
EP 22 20 7599

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Place of search	Date of completion of the search	Examiner
The Hague	14 April 2023	Ruiz Martínez, C

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