

PROCESS AND SYSTEM FOR PRODUCING HYDROCARBONS HAVING BIOGENIC CARBON CONTENT, A SAMPLE TREATMENT AND ANALYSIS SYSTEM AND USE THEREOF

TECHNICAL FIELD

- 5 The present disclosure generally relates to a process and system for producing hydrocarbons having biogenic carbon content. The disclosure relates particularly, though not exclusively, to a process and system for producing hydrocarbons involving a convenient and safe way to determine biogenic carbon content in a conversion unit's gaseous output stream comprising H₂S, preferably in all output streams of a conversion unit of a refinery.
- 10 Also a sample treatment and analysis system is disclosed, as well as its use in a process for producing hydrocarbons having biogenic carbon content.

BACKGROUND

This section illustrates useful background information without admission of any technique described herein representative of the state of the art.

- 15 There is an ongoing need to reduce greenhouse gas (GHG) emissions and/or carbon footprint in the transportation and petrochemical industry. At the same time the demand for hydrocarbons in these and other fields increases worldwide, and the crude oil reserves are vanishing. Accordingly, interest towards the use of sustainable materials in hydrocarbon production is growing.
- 20 Fully biobased alternatives for drop-in replacements of fossil hydrocarbon products have been successfully created. For example Neste MY Renewable Diesel is a Hydrotreated Vegetable Oil (HVO) developed by Neste Corporation. It is made by NEXBTL™ process, which is a proprietary HVO process of Neste Corporation, from 100% renewable raw materials such as waste and residues, and results in as much as 75-95% less greenhouse
- 25 gas (GHG) emissions over the fuel's life cycle when compared with fossil diesel. Renewable Neste RE™, on the other hand, is a 100% renewable feedstock of Neste Corporation showing a GHG emission reduction of more than 85% over the life cycle when used to replace conventional fossil feedstock in the chemical and polymers industry.

- In addition to concepts dedicated for processing fully biogenic feeds, for tackling the above-
- 30 mentioned challenges further approaches for industrial processes and products are urgently

needed. In this regard, co-feeding of biomass-derived streams into existing petroleum refineries has a growing interest not least because of the existing infrastructure, allowing almost instant implementation. When co-processing biogenic feedstocks with fossil feedstocks, the biogenic carbon content distributes unequally between the various output/product streams and hence different approaches have been developed to calculate the amount of the bio-output. For example, the International Sustainability and Carbon Certification (ISCC) has established a co-processing certification providing three different approaches for calculating the bio-yield: energetic determination; determination through the efficiency/losses of a process; and 12C/14C analyses. For all three approaches, the determined sustainable bio-output can then be attributed to the respective products. 12C/14C analysis is also one of four options offered by ISCC's certification scheme ISCC PLUS for conducting the mass balancing for a certified processing unit and for determining the sustainable output.

WO2021100004A1 discloses a method to determine renewable carbon content while co-processing biogenic feedstocks in a refinery environment during the production of renewable fuels. The proposed approach involves analyzing samples of liquid feedstocks and products collected from fixed sampling points of a petroleum coprocessing operation with a triple to double coincidence ratio (TDCR) scintillation counter. The proposed approach is said to reduce the total number of downstream measurements typically required when determining bio-based carbon content in a refinery co-processing petroleum and bio-based feedstocks and to provide a lower detection limit that can provide more accurate measurements e.g. compared to AMS at low blending levels of a bio-component. For determining renewable carbon content in carbon-bearing refinery gas, such as fuel gas, WO2021100004A1 generally suggests using AMS, however without closer guidance.

Evidently, there is a continuous need to develop improvements in co-processing, particularly providing practical solutions to determine the biogenic carbon content in various refinery streams and products, including gaseous streams, even gaseous streams containing hazardous species such as H₂S.

SUMMARY

It is an aim to solve or alleviate at least some of the problems related to prior art, including reducing GHG emissions and dependence from petroleum sources, especially in the transportation and petrochemicals sectors. An aim is to provide hydrocarbons having biogenic carbon content by co-processing feeds having biogenic and non-biogenic carbon

content. Another aim is to provide a convenient and safe approach for determining biogenic carbon content in a gaseous or gas-containing output stream of a refinery unit, even when containing hazardous species such as H₂S. A further aim is to improve the overall economy of co-processing and/or the overall value of a product slate of a co-processing unit.

- 5 The appended claims define the scope of protection. Any examples and technical descriptions of apparatuses, systems, products and/or methods in the description and/or drawings not covered by the claims are presented as examples useful for understanding the invention.

- 10 Hydrogen sulfide (H₂S) is a highly irritating, odorous, and toxic gas that is hazardous even at low concentrations. It irritates the eyes and airways after prolonged exposure at about 5 ppm and causes instant death at 1000–2000 ppm. H₂S is commonly present in the gaseous effluent streams of various refinery units, and its removal from the refinery gases is required both for economic and safety reasons. Removal of H₂S and other sour gases such as CO₂, is commonly called sweetening. It would be convenient to determine the biogenic carbon
15 content in a gaseous stream of a refinery unit only after (i.e. downstream of) the sweetening treatment, so as to avoid or reduce risks associated with handling a sample of the gaseous stream. However, after the sweetening treatment part of the biogenic carbon content is lost as sweetening removes also biogenic CO₂, and also some biogenic CO may be lost during sweetening. Furthermore, to reduce investment and operating costs, it would be desired to
20 utilise a common sweetening unit for treating gaseous streams from several conversion units of a refinery. On the other hand, e.g. for an ISCC PLUS certification it is required that the mass balancing, and biogenic carbon content determination in a gaseous output, is conducted for an individual conversion unit of a refinery, so determining the biogenic carbon content in the sweetened mixture of gases from several refinery units may not be helpful.
25 Additionally, even if measuring the biogenic carbon content in such sweetened mixture of gases from several refinery units would add value of this combined gas stream, the biogenic carbon content might get too diluted for its measurement, e.g. if the share of biobased feed co-processed in an individual unit is low and/or the gaseous stream of a bio-co-processing unit is combined with high volumes of gaseous streams from conversion units processing
30 fossil feeds, only.

The process according to the first example aspect and the system according to the second example aspect, as specified in the following, allow to reduce GHG emissions and dependence from petroleum sources, especially in the transportation and petrochemicals sectors, by providing hydrocarbons having biogenic carbon content by co-processing feeds

having biogenic and non-biogenic carbon content. The sample treatment and analysis system according to the third example aspect, as specified in the following, provides a convenient and safe approach for determining biogenic carbon content in a gaseous or gas-containing liquid stream comprising H₂S and at least one or more of carbon oxide(s) and/or C1-C3 hydrocarbons, especially for use in the process according to the first example aspect. Furthermore, the present disclosure provides a convenient and safe way to conduct the mass balancing, and biogenic carbon content determination in an output stream, for individual conversion units of a refinery, as required e.g. for an ISCC PLUS certification.

According to a first example aspect, there is provided a process for producing hydrocarbons having biogenic carbon content, the process comprising:

- a) providing a refinery feed having biogenic carbon content, non-biogenic carbon content and sulphur content;
- b) refining the refinery feed in a conversion unit to obtain a conversion effluent comprising at least H₂S and hydrocarbons, and preferably also carbon oxide(s);
- c) subjecting the conversion effluent to separation in a separation section to obtain a gaseous stream comprising H₂S and at least one or more of carbon oxide(s) and/or C1-C3 hydrocarbons, and a degassed hydrocarbon stream;
- d) subjecting the gaseous stream to a sweetening treatment to obtain a sweetened gas stream; and
- e1) collecting an aliquot of the gaseous stream as a sample before subjecting the gaseous stream to the sweetening treatment,
- e2) subjecting the sample to a selective H₂S removal treatment to obtain a selectively H₂S depleted sample,
- e3) optionally subjecting the selectively H₂S depleted sample to drying to obtain a dehydrated sample, and
- e4) subjecting at least a portion of the selectively H₂S depleted and optionally dehydrated sample to a biogenic carbon content determination, preferably using accelerator mass spectrometry (AMS) technique, to obtain the content of biogenic carbon in the gaseous stream; and
- f) optionally further separating from the degassed hydrocarbon stream at least one or more distillate(s), and a fractionation bottom.

According to a second example aspect a system for producing hydrocarbons having biogenic carbon content is provided, the system comprising:

- a) at least one or more refinery feed tank(s) configured to receive a refinery feed having biogenic carbon content, non-biogenic carbon content and sulphur content, or components of the refinery feed;
- b) a conversion unit in fluid communication with the refinery feed tank(s), and configured to receive and refine the refinery feed to obtain a conversion effluent comprising at least H₂S and hydrocarbons, and preferably also carbon oxide(s);
- c) a separation section in fluid communication with the conversion unit and configured to receive the conversion effluent and to separate therefrom a gaseous stream and optionally an unstabilised naphtha stream both comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons, and a degassed hydrocarbon stream, wherein the separation section is optionally further configured to separate from the degassed hydrocarbon stream at least one or more distillate(s) and a fractionation bottom;
- d) a sweetening unit in fluid communication with the separation section and configured to receive and sweeten the gaseous stream to obtain a sweetened gas stream; and
- e) a sample treatment and analysis system comprising:
 - e1) a sampler in communication, preferably in fluid communication, with the separation section and configured to collect as a sample an aliquot of the gaseous stream at a location upstream of the sweetening unit,
 - e2) a selective H₂S removal unit in communication, preferably in fluid communication, with the sampler and configured to receive the sample and to selectively remove H₂S from the sample to obtain a selectively H₂S depleted sample,
 - e3) an optional drying unit in communication, preferably in fluid communication, with the selective H₂S removal unit and configured to receive and dehydrate the selectively H₂S depleted sample to obtain a dehydrated sample, and an optional gas chromatography (GC) analyzer in communication, preferably in fluid communication, with the selective H₂S removal unit optionally via the drying unit and configured to receive a portion of the selectively H₂S depleted and optionally dehydrated sample, and
 - e4) a biogenic carbon content analyzer, preferably using accelerator mass spectrometry (AMS) technique, in communication, preferably in fluid communication, with the selective H₂S removal unit optionally via the drying unit, and configured to

receive at least a portion of the selectively H₂S depleted and optionally dehydrated sample and to determine its biogenic carbon content to obtain the content of biogenic carbon in the gaseous stream.

According to a third example aspect a sample treatment and analysis system is provided,
5 the system comprising:

- e1) a sampler configured to collect a sample comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons,
- e2) a selective H₂S removal unit in communication, preferably in fluid communication, with the sampler and configured to receive the sample and to selectively remove H₂S from the
10 sample to obtain a selectively H₂S depleted sample,
- e3) an optional drying unit in communication, preferably in fluid communication, with the selective H₂S removal unit and configured to receive and dehydrate the selectively H₂S depleted sample to obtain a dehydrated sample, and an optional gas chromatography (GC) analyzer in communication, preferably in fluid communication, with the selective H₂S
15 removal unit optionally via the drying unit and configured to receive a portion of the selectively H₂S depleted and optionally dehydrated sample, and
- e4) a biogenic carbon content analyzer, preferably using accelerator mass spectrometry (AMS) technique, in communication, preferably in fluid communication, with the selective H₂S removal unit optionally via the drying unit, and configured to receive at least a portion
20 of the selectively H₂S depleted and optionally dehydrated sample and to determine its biogenic carbon content to obtain the content of biogenic carbon in the collected sample.

According to a fourth example aspect there is provided use of a system for producing hydrocarbons having biogenic carbon content according to the second example aspect, or of a sample treatment and analysis system according to the third example aspect, in a
25 process for producing hydrocarbons having biogenic and non-biogenic carbon content, preferably in a process according to the first example aspect.

According to a fifth example aspect there is provided use of a sample treatment and analysis system according to the third example aspect for creating and/or training a model for estimating biogenic carbon content of a gaseous stream and/or of an unstabilised naphtha
30 stream in a process for producing hydrocarbons having biogenic carbon content, wherein the gaseous stream and the unstabilised naphtha stream both comprise H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons and are obtainable by separating from a conversion effluent obtained by refining in a conversion unit a refinery

feed having biogenic carbon content, non-biogenic carbon content and sulphur content; preferably for creating and/or training a model for estimating biogenic carbon content of a gaseous stream and/or of an unstabilised naphtha stream in a process according to the first example aspect.

- 5 Different non-binding example aspects and embodiments have been illustrated in the foregoing. The embodiments in the foregoing are used merely to explain selected aspects or steps that may be utilised in different implementations. Some embodiments may be presented only with reference to certain example aspects. It should be appreciated that corresponding embodiments may apply to other example aspects as well.

10 BRIEF DESCRIPTION OF THE FIGURES

Some example embodiments will be described with reference to the accompanying figures, in which:

Fig. 1 schematically shows a sample treatment and analysis system according to an example embodiment of the present disclosure; and

- 15 Fig. 2 schematically shows a process and/or a system for producing hydrocarbons having biogenic carbon content according to an example embodiment of the present disclosure.

DETAILED DESCRIPTION

- 20 In the following description, like reference signs denote like elements or steps. All standards referred to herein are the latest revisions available at the filing date, unless otherwise mentioned.

As used herein, carbon oxide(s) refer to carbon monoxide (CO) and/or carbon dioxide (CO₂).

- 25 As used herein hydrocarbons refer to compounds consisting of carbon and hydrogen, including paraffins, n-paraffins, i-paraffins, monobranched i-paraffins, multibranched i-paraffins, olefins, naphthenes, and aromatics. Oxygenated hydrocarbons refer herein to hydrocarbons comprising covalently bound oxygen.

Chemically, the biogenic (renewable) or non-biogenic (non-renewable) origin of any organic compound, including hydrocarbons, can be determined by suitable method for analysing the content of carbon from renewable sources e.g. DIN 51637:2014-02, ASTM D6866-2022,

or EN 16640:2017. Said methods are based on the fact that carbon atoms of renewable or biological origin comprise a higher number of unstable radiocarbon (^{14}C) atoms compared to carbon atoms of fossil origin. Therefore, it is possible to distinguish between carbon compounds derived from renewable or biological sources and carbon compounds derived from non-renewable (such as petroleum) sources by analysing the ratio of ^{12}C and ^{14}C isotopes. Thus, a particular ratio of said isotopes can be used as a "tag" to identify a renewable carbon compound and differentiate it from non-renewable carbon compounds. The isotope ratio does not change in the course of chemical reactions. Therefore, the isotope ratio can be used for identifying renewable carbon compounds and distinguishing them from non-renewable carbon compounds in feeds, refining feeds, co-feeds, fractions, or compositions, or various blends thereof. In the present disclosure, biogenic carbon content refers to biogenic carbon content expressed as the amount of biogenic carbon in the material as a weight percent of the total carbon (TC) in the material (as may be determined e.g. in accordance with ASTM D6866-2022 or EN 16640:2017), unless otherwise stated.

As used herein, the term circular in connection with content or materials such as (co-)feeds, fractions, or compositions refers to content or material that is based on or contains reused and/or recycled non-biogenic carbon, but that may additionally contain biogenic carbon. Typical exemplary sources for reused and/or recycled non-biogenic carbon, possibly also containing at least some biogenic carbon, include reclaimed organic commodities, especially waste plastics, end of life tires, used lubricants, and/or municipal solid waste.

Renewable, circular, and petroleum content, materials, (co-)feeds, fractions, or compositions are considered differing from one another based on their origin and impact on environmental issues. Therefore, they may be treated differently under legislation and regulatory framework. Typically, renewable, circular, and petroleum materials etc. are differentiated based on their origin and information thereof provided by the producer.

In the context of this disclosure, CX hydrocarbons, paraffins, or similar, refer to hydrocarbons, paraffins, or similar, respectively, having a carbon number of at least X, where X is any feasible integer; CX-CY (or CX to CY) hydrocarbons, paraffins, or similar, refer to at least hydrocarbons, paraffins, or similar, respectively, having a carbon number of at least X and at most Y. It is understood that every compound having a carbon number falling within the definition is not necessarily present, and that also compounds having a carbon number falling outside the definition may be present.

According to a first example aspect, there is provided a process for producing hydrocarbons having biogenic carbon content, the process comprising:

- a) providing a refinery feed having biogenic carbon content, non-biogenic carbon content and sulphur content;
- 5 b) refining the refinery feed in a conversion unit to obtain a conversion effluent comprising at least H₂S and hydrocarbons, and preferably also carbon oxide(s);
- c) subjecting the conversion effluent to separation in a separation section to obtain a gaseous stream comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons, and a degassed hydrocarbon stream;
- 10 d) subjecting the gaseous stream to a sweetening treatment to obtain a sweetened gas stream; and
 - e1) collecting an aliquot of the gaseous stream as a sample before subjecting the gaseous stream to the sweetening treatment,
 - e2) subjecting the sample to a selective H₂S removal treatment to obtain a selectively
15 H₂S depleted sample,
 - e3) optionally subjecting the selectively H₂S depleted sample to drying to obtain a dehydrated sample, and
 - e4) subjecting at least a portion of the selectively H₂S depleted and optionally dehydrated sample to a biogenic carbon content determination, preferably using
20 accelerator mass spectrometry (AMS) technique, to obtain the content of biogenic carbon in the gaseous stream; and
- f) optionally further separating from the degassed hydrocarbon stream at least one or more distillate(s), and a fractionation bottom.

25 Hydrogen sulfide (H₂S) is a highly irritating, odorous, and toxic gas that is hazardous even at low concentrations. It irritates the eyes and airways after prolonged exposure at about 5 ppm and causes instant death at 1000–2000 ppm. The inherent tendency of H₂S to form an acidic solution in the presence of water may lead to corrosion in equipment and pipelines causing safety issues at refineries. Its presence may also reduce the heating value of fuel gases, its combustion leading to the emission of sulfur dioxide and other harmful sulfur
30 oxides. Its presence may also lead to poisoning of certain catalysts. Since H₂S is commonly present in the gaseous effluent streams of various refinery units, its removal from the refinery gases is required both for economic and safety reasons.

Removal of H₂S and other sour gases such as CO₂, is commonly called sweetening. It would be convenient to determine the biogenic carbon content in a gaseous stream of a refinery unit only after (i.e. downstream of) the sweetening treatment, so as to avoid or reduce risks associated with handling a sample of gaseous stream containing H₂S.

5 However, in the sweetening treatment part of the biogenic carbon content is lost as sweetening removes also biogenic CO₂, and may also remove some CO. Furthermore, to reduce investment and operating costs, it would be desired to utilise a common sweetening unit for treating gaseous streams from several refinery units of a refinery. On the other hand, e.g. for an ISCC PLUS certification it is required that the mass balancing, and biogenic
10 carbon content determination in all output streams, including the gaseous output stream, is conducted for an individual conversion unit of a refinery, so determining the biogenic carbon content in the sweetened mixture of gases from several refinery units would not be helpful. Additionally, even if measuring the biogenic carbon content in such sweetened mixture of gases from several refinery units would add value of this combined gas stream, the biogenic
15 carbon content might get too diluted for its measurement, e.g. if the share of biobased feed co-processed in an individual unit is low and/or the gaseous stream of a bio-co-processing unit is combined with high volumes of gaseous streams from conversion units processing fossil feeds, only.

The process according to the first example aspect and the system according to the second
20 example aspect, as specified in the following, allow to reduce GHG emissions and dependence from petroleum sources, especially in the transportation and petrochemicals sectors, by providing hydrocarbons having biogenic carbon content, by processing feeds having biogenic and non-biogenic carbon content. The present inventors found that by utilising a sample treatment and analysis system e.g. as specified in the third example
25 aspect, the biogenic carbon content in the gaseous output stream of an individual conversion unit may be determined in a convenient and safe way, despite the H₂S content of the gaseous stream, and essentially without losing any of the biogenic carbon content of the gaseous stream. This is advantageous in the process and system for producing hydrocarbons having biogenic carbon content of the present disclosure, allowing to
30 determine the actual biogenic carbon content in a gaseous output stream of an individual conversion unit of a refinery, as may be required e.g. for an ISCC PLUS certification.

In the separation section also a gas-containing liquid stream, particularly an unstabilised naphtha stream, sometimes referred to as wild naphtha, may be separated. Such unstabilised naphtha stream may have significant content of residual gases in addition to
35 naphtha boiling range liquid hydrocarbons, these gases typically comprising H₂S and at

least one or more of carbon oxide(s) and/or C1-C3 hydrocarbons. The unstabilised naphtha stream may be separated from the conversion effluent, preferably after separating gaseous stream(s), for example using a stripper where also the degassed hydrocarbon stream may be obtained. The biphasic nature of the unstabilised naphtha adds an additional challenge to the biogenic carbon content determination. For example, the gas-phase and the liquid phase of such biphasic sample may behave differently, such as proceed at different rates, in the sample preparation and/or biogenic carbon content determination in the biogenic carbon content analyzer, and also in the preceding treatment steps, such as in the selective H₂S removal treatment of the present disclosure. This may lead to inaccuracies or errors in the biogenic carbon content determination in step e4). However, the present inventors realised that biphasic samples can be managed in embodiments of the present process and systems by subjecting an aliquot of the unstabilised naphtha stream as a (unstabilised) naphtha sample to i) phase separation or to ii) high pressure compression before biogenic carbon content determination, as discussed in the following.

The i) phase separation of the naphtha sample into a liquid naphtha sample and a gas-phase sample may be conducted for example by letting the naphtha sample collected in a container to achieve equilibrium under controlled conditions in the container, and collecting the head-space phase as the gas-phase sample and the liquid phase as the liquid naphtha sample. If desired, the naphtha sample may be subjected to a composition analysis using gas chromatography (GC) before the phase separation. For that, a portion of the naphtha sample may be liquefied by subjecting to high pressure compression, for example by pressurising a container containing the naphtha sample with an inert gas, to get all components of the naphtha sample in liquid state. For complete liquefaction, the pressure, such as the pressure of the inert gas, should be sufficiently high, preferably at least 13.8 bar higher than the vapour pressure of the naphtha sample at the container temperature. After the phase separation, the gas-phase sample is subjected to a procedure according to steps e2) to e4) to obtain the content of biogenic carbon in the gas-phase sample, while the biogenic carbon content in the liquid naphtha sample may be determined in any conventional way, preferably using AMS technique. For example, the same biogenic carbon content analyzer as for the gas-phase sample may be utilised. The biogenic carbon content in the unstabilised naphtha stream may then be back-calculated based on the contents of biogenic carbon in the gas-phase sample and in the liquid naphtha sample. For said calculation, the share of the gas-phase sample and the liquid naphtha sample in the naphtha sample is typically also needed, and may be determined for example based on a composition analysis of the naphtha sample and identifying compounds that should be in

the gas-phase and compounds that should be in the liquid phase, composition analyses conducted on the gas-phase sample and the liquid naphtha sample separately, measured wt.-% share or vol.-% share of the gas-phase sample and the liquid naphtha sample in the naphtha sample, or any combination thereof. Correspondingly, the sample treatment and analysis system may further comprise respective means for determining the share of the gas-phase sample and the liquid naphtha sample in the naphtha sample.

The ii) high pressure compression of the naphtha sample to obtain a liquefied sample may be conducted by pressurising a container containing the naphtha sample with an inert gas, to get all components of the naphtha sample in liquid state. For complete liquefaction, the pressure, such as the pressure of the inert gas, should be sufficiently high, preferably at least 13.8 bar higher than the vapour pressure of the naphtha sample at the container temperature. By liquefying the biphasic sample, different behaviour of the normally gaseous and normally liquid compounds in the sample treatment and analysis steps e1) to e4) may be minimised or avoided, thereby minimising also inaccuracies or errors in the biogenic carbon content determination. By configuring the system suitably, the liquefied sample may be maintained in the liquefied state until fed to the biogenic carbon content analyzer/determination in step e4).

Hence, in certain preferred embodiments the separation in step c) further includes separating an unstabilised naphtha stream comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons, and the process further comprises collecting an aliquot of the unstabilised naphtha stream as a naphtha sample, and i) subjecting the naphtha sample to phase separation to obtain a gas-phase sample and a liquid naphtha sample, subjecting the gas-phase sample to a procedure according to steps e2) to e4) to obtain the content of biogenic carbon in the gas-phase sample, subjecting the liquid naphtha sample to a biogenic carbon content determination, preferably using accelerator mass spectrometry (AMS) technique, to obtain the content of biogenic carbon in the liquid naphtha sample, and calculating the biogenic carbon content in the unstabilised naphtha stream based on the contents of biogenic carbon in the gas-phase sample and in the liquid naphtha sample; or ii) subjecting the naphtha sample to high pressure compression to obtain a liquefied sample, and subjecting the liquefied sample to a procedure according to steps e2) to e4) to obtain the content of biogenic carbon in the unstabilised naphtha stream.

Also in these embodiments, composition analysis using gas chromatography (GC) may be utilised to verify integrity of the sample treatment and analysis steps e1) to e4), selectivity of the H₂S removal step e2) etc.

- There are several ways to provide the refinery feed having biogenic carbon content, non-biogenic carbon content and sulphur content. Such refinery feeds may be obtained for example by combining refinery feed components, wherein at least one refinery feed component has biogenic carbon content, at least one refinery feed component has non-biogenic carbon content, and at least one refinery feed component has sulphur content. Such refinery feeds may also be obtained by combining refinery feed components, wherein at least one refinery feed component has biogenic and non-biogenic carbon content, and at least one refinery feed component has sulphur content, or wherein at least one refinery feed component has biogenic carbon content, and at least one refinery feed component has non-biogenic carbon content and sulphur content. Some refinery feed components may have biogenic and non-biogenic carbon content, as well as sulphur content, and could be utilised alone as the refinery feed. At least part of the sulphur content of the refinery feed may originate from sulphur compounds with which the feed may be spiked to maintain a catalyst optionally used e.g. in catalytic conversion units sufficiently sulphided and active.
- Examples of refinery feed components having at least biogenic carbon content include vegetable oil(s), animal fat(s), microbial oil(s), lignocellulose-derived biocrude(s), used lubricating oil(s) having biogenic carbon content, and/or liquefied organic waste having biogenic carbon content. Typical vegetable oil(s), animal fat(s), microbial oil(s), lignocellulose-derived biocrude(s), used lubricating oil(s) having biogenic carbon content, and/or liquefied organic waste having biogenic carbon content may contain for example fatty acid(s), fatty acid glyceride(s), fatty acid alkyl ester(s), fatty alcohol(s), resin acid(s), resin ester(s), other oxygenated hydrocarbons, olefins, and/or cyclic hydrocarbons. Exemplary vegetable oil(s) usable in the present process and system include rapeseed oil, canola oil, soybean oil, coconut oil, sunflower oil, palm oil, palm kernel oil, peanut oil, linseed oil, sesame oil, maize oil, poppy seed oil, cottonseed oil, soy oil, tall oil, crude tall oil (CTO), corn oil, castor oil, jatropha oil, jojoba oil, olive oil, flaxseed oil, camelina oil, safflower oil, babassu oil, seed oil of any of Brassica species or subspecies, such as Brassica carinata seed oil, Brassica juncea seed oil, Brassica oleracea seed oil, Brassica nigra seed oil, Brassica napus seed oil, Brassica rapa seed oil, Brassica hirta seed oil and Brassica alba seed oil, and rice bran oil, and/or fractions or residues of said vegetable oils such as palm olein, palm stearin, palm fatty acid distillate (PFAD), purified tall oil, tall oil fatty acids, tall oil resin acids, distilled tall oil, tall oil unsaponifiables, tall oil pitch (TOP), and/or used cooking oils of vegetable origin; exemplary animal fats may include tallow, lard, yellow grease, brown grease, fish fat, poultry fat, and/or used cooking oil of animal origin; and exemplary microbial oils may include algal lipids, fungal lipids, and/or bacterial lipids. The

lignocellulose-derived biocrude(s) may comprise thermally such as hydrothermally or by pyrolysis, or catalytically such as thermo-catalytically liquefied lignocellulosics, wherein exemplary lignocellulosics may include woody biomass and residues such as wood chips, sawdust, forestry thinnings, road cuttings, bark, branches, garden and park residues and weeds, energy crops like coppice, willow, miscanthus, and giant reed; agricultural (by)products such as grasses, straw, stems, stover, husk, cobs and shells from e.g. wheat, rye, corn rice and/or sunflowers, empty fruit bunches from palm oil production, palm oil manufacturers effluent, residues from sugar production such as bagasse, vinasses, molasses and/or greenhouse wastes, energy crops like miscanthus, switchgrass, sorghum, and/or jatropha; and/or lignocellulosic industrial side streams such as paper sludges, off-specification fibres from paper production, residues and byproducts from food production such as juice or wine production, vegetable oil production, restaurant wastes.

The used lubricating oil(s) having biogenic carbon content may comprise engine oils, driveline fluids, greases, hydraulic fluids, gear oils, switchgear oils, transformer oils, metal-cutting fluids, wherein the biogenic carbon content may originate for example from ester oils, glyceridic oils, and/or HVO. The liquefied organic waste having biogenic carbon content may comprise thermally such as hydrothermally or by pyrolysis, or catalytically such as thermo-catalytically liquefied organic waste having biogenic carbon content, wherein the organic waste having biogenic carbon content may comprise waste plastics (containing e.g. some bio-based plastics), end of life tires (ELT, containing e.g. natural rubber), and/or municipal solid waste (MSW, containing e.g. biomass waste). Evidently, due to its mixed waste nature, the liquefied organic waste having biogenic carbon content typically also has non-biogenic carbon content, i.e. the liquefied organic waste may have both biogenic and non-biogenic carbon content. For example the biogenic carbon content of MSW may vary greatly, but is typically significant, such as from 40 to 70 wt.-%, based on the total weight of carbon (TC) in the MSW. Also the biogenic carbon content of ELT may vary, but is typically significant, such as from 15 to 40 wt.-%, based on the total weight of carbon (TC) in the ELT. Also the biogenic carbon content of liquefied waste plastics may vary, but is currently foreseen much lower than the share of non-biogenic carbon content, however this may change over time when the availability of bio-based plastics increases.

If the at least one or more of vegetable oil(s), animal fat(s), microbial oil(s), lignocellulose-derived biocrude(s), used lubricating oil(s) having biogenic and/or non-biogenic carbon content, and/or liquefied organic waste having biogenic and/or non-biogenic carbon content contain amounts or species of impurities that are not tolerated or preferred when refining in the conversion unit, the content of said impurities may be reduced to acceptable limits using

pre-treatment methods known in the art. Exemplary pre-treatment methods suitable for the present disclosure comprise treating with mineral acids, degumming, treating with hydrogen, heat treating, deodorizing, washing with water, treating with base, demetallation, distillation, removal of solids, bleaching, and any combinations thereof.

- 5 Examples of refinery feed components having at least non-biogenic carbon content include various fossil feeds such as petroleum feeds, used lubricating oils having non-biogenic carbon content, and liquefied organic waste having non-biogenic carbon content, whereof the two latter mentioned - as explained above - may also have biogenic carbon content. Especially used lubricating oils, and thermally such as hydrothermally or by pyrolysis, or
10 catalytically such as thermo-catalytically liquefied organic waste comprising waste plastics or ELT may have high non-biogenic carbon content.

The above examples of refinery feed components having at least non-biogenic carbon content are also examples of refinery feed components that may have even significant sulphur content. However, also some of the above examples of refinery feed components
15 having biogenic carbon content, such as tall oil or fractions or residues thereof, may have significant sulphur content, hence leading to H₂S formation when refining in a conversion unit.

In certain embodiments, the refinery feed may consist of used lubricating oils and/or liquefied organic waste, having biogenic and non-biogenic carbon content, as these typically
20 also have some sulphur content.

However, in certain preferred embodiments wherein the refinery feed comprises at least one or more of vegetable oil(s), animal fat(s), microbial oil(s), lignocellulose-derived biocrude(s), used lubricating oil(s) having biogenic carbon content, and/or liquefied organic waste having biogenic carbon content, and at least one or more of petroleum feed(s), used
25 lubricating oil(s) having non-biogenic carbon content, and/or liquefied organic waste having non-biogenic carbon content. These two refinery feed (component) groups represent components typically having at least biogenic carbon content, and at least non-biogenic carbon content and sulphur content, respectively. More preferably the refinery feed comprises at least one or more of vegetable oil(s), animal fat(s), microbial oil(s), and/or
30 lignocellulose-derived biocrude(s) - these representing biogenic refinery components that are well-available, suitable for co-processing, and require refining e.g. due to the relatively high oxygen content, to form high-value hydrocarbon products - and at least one or more petroleum feed(s), that are vanishing and are hence beneficially partially substituted with

biogenic materials. When utilising these refinery feed components, the benefits of the present process and systems may be seen as highest, as the thus-obtained gaseous stream is foreseen to have significant contents of H₂S and biogenic CO₂. In certain further preferred embodiments, the refinery feed comprises at least one or more of vegetable oil(s), animal fat(s), and/or microbial oil(s), and at least one or more petroleum feed(s). Presence of the lipidic co-feeds, typically rich in glycerides, provide the additional benefit of the glycerol-backbone forming biogenic propane particularly when subjected to hydroprocessing, which biogenic propane ends up in the gaseous stream, and is captured when using the present process or system(s).

- 10 Particularly preferably the refinery feed comprises - as at least one refinery feed component having non-biogenic carbon content and sulphur content - at least one or more petroleum feed(s). In certain embodiments, the petroleum feed(s) comprise at least one or more of atmospheric distillate(s); atmospheric distillation bottom(s); vacuum distillate(s); distillate(s) of (hydro)cracked distillation bottom(s); atmospheric bottom(s) of (hydro)cracked distillation
- 15 bottom(s); distillate(s) of (hydro)cracked vacuum distillate(s); and/or atmospheric bottom(s) of (hydro)cracked vacuum distillate(s), of a petroleum crude oil. The choice of the petroleum feed is not particularly limited, but components of lesser quality and/or having limited utility in high value applications may be preferred e.g. over straight-run petroleum distillates. In this way, the overall value of a product slate of an entire refinery may be optimised. Hence,
- 20 in certain preferred embodiments, the petroleum feed comprises at least one or more of atmospheric distillation bottom(s); vacuum distillate(s); atmospheric and/or vacuum distillate(s) of (hydro)cracked atmospheric and/or vacuum distillation bottom(s); atmospheric distillation bottom(s) of (hydro)cracked atmospheric and/or vacuum distillation bottom(s); atmospheric and/or vacuum distillate(s) of (hydro)cracked vacuum distillate(s); and/or atmospheric bottom(s) of (hydro)cracked vacuum distillate(s), of a petroleum crude oil.
- 25

- The biogenic carbon content of the refinery feed may vary within broad ranges, typically being from 1 to 99 wt.-%, based on the total weight of carbon (TC) in the refinery feed (EN 16640:2017). In certain preferred embodiments, the refinery feed has biogenic carbon
- 30 content within a range from 1 to 95 wt.-%, preferably from 3 to 90 wt.-%, more preferably from 3 to 80 wt.-%, even more preferably from 5 to 50 wt.-%, based on the total weight of carbon (TC) in the refinery feed (EN 16640:2017). When the biogenic carbon content of the refinery feed is within these ranges, due to the nature of the refinery feed components having at least biogenic carbon, and the nature of the refinery feed components having at
- 35 least non-biogenic carbon, the content of H₂S and CO₂ in the gaseous stream separated

from the conversion effluent are such that the benefits of the present process and systems may be seen as highest: the gaseous stream has well detectable biogenic carbon content, and contain also biogenic CO₂, and typically also significant H₂S content.

Also the total sulphur content of the refinery feed may vary within broad ranges, typically being at least 0.05 wt.-%, preferably at least 0.1 wt.-%, more preferably at least 0.2 wt.-%, typically within a range from 0.05 wt.-% to 2 wt.-%, preferably from 0.1 wt.-% to 2 wt.-%, more preferably from 0.2 wt.-% to 1 wt.-%, based on the total weight of the refinery feed (ASTM D7039-15a(2020)). The sulphur content of the refinery feed is known to have an influence on the deoxygenation mechanism. Already when the sulphur content of the refinery feed is somewhat elevated, such as at least 0.05 wt.-%, or more typically - especially when using petroleum feed(s) as refinery feed component(s) - at least 0.1 wt.-%, preferably at least 0.2 wt.-%, based on the total weight of the refinery feed (ASTM D7039-15a(2020)), the oxygen atom cleavage, i.e. deoxygenation, via decarboxylation and decarbonylation reactions may get more and more favoured over hydrodeoxygenation, thereby providing higher carbon oxide content in the gaseous stream. Since oxygen atoms are typically abundant in refinery feed components having at least biogenic carbon content, particularly in vegetable oil(s), animal fat(s), microbial oil(s), and/or lignocellulose-derived biocrude(s), the carbon in CO₂ molecules present in the gaseous stream is largely biogenic and hence the present process and systems are particularly advantageous as capturing this content.

Also the oxygen content of the refinery feed may vary within broad ranges, typically being at least 0.1 wt.-%, preferably at least 0.5 wt.-%, more preferably at least 1 wt.-%, typically within a range from 0.1 wt.-% to 15 wt.-%, preferably from 0.5 wt.-% to 10 wt.-%, more preferably from 1 wt.-% to 8 wt.-%, based on the total weight of the refinery feed (ASTM D5622-2017).

When the refinery feed having biogenic carbon content, non-biogenic carbon content and sulphur content is refined in a conversion unit, heteroatoms covalently bound in organic compounds, particularly oxygen atoms typically abundant in refinery feed components having at least biogenic carbon content, and sulphur atoms typically abundant in refinery feed components having at least non-biogenic content, are cleaved forming H₂S and carbon oxides. At the same time hydrocarbons are formed, typically both hydrocarbons that are gaseous at NTP, such as C₁-C₃ hydrocarbons, and hydrocarbons that are not gaseous at NTP, but e.g. liquid. While formation of hazardous H₂S may be seen as undesired, cleavage of sulphur from the feed components is necessary to obtain low-sulphur

hydrocarbons meeting requirements for various uses such as for use in fuels. In refinery conversion processes this typically leads to H₂S formation. Additionally, refinery feed components having sulphur content may also be process-wise beneficial, for example for keeping a catalyst optionally utilised in a conversion unit sufficiently sulphided and hence
5 active, even without separate sulphur spiking.

In the present process and system, the refinery feed is refined in a conversion unit to obtain a conversion effluent comprising at least H₂S and hydrocarbons, and preferably carbon oxide(s). The refining may be arranged in a single refining stage or it may comprise multiple refining stages arranged in multiple refining zones in a conversion unit. In other words, the
10 refining may comprise e.g. catalytic hydroprocessing, catalytic cracking, and/or thermal cracking arranged in catalytic hydroprocessing zone(s), catalytic cracking zone(s), and/or thermal cracking zone(s) in a conversion unit. Whether the refining in the conversion unit is arranged in a single refining stage or multiple refining stages in multiple refining zones, these refining stages or zones may be arranged in one or more reactors. The number of
15 reactors is a matter of engineering, and may be influenced by practical issues such as maximum height of the facility at the site, reactor diameter, regulatory and maintenance issues at the site, wind conditions at the site, and/or available equipment.

In certain preferred embodiments, the refining includes at least one or more of catalytic hydroprocessing, catalytic cracking, and/or thermal cracking, preferably at least catalytic
20 hydroprocessing, more preferably catalytic hydroprocessing comprising at least catalytic hydrotreatment. In these embodiments the conversion unit may comprise one or more catalytic hydroprocessing zone(s), catalytic cracking zone(s), or thermal cracking zone(s). All these refining types are well known, and include technologies capable of cleaving heteroatoms from organic compounds. When using only one refining type in a conversion
25 unit, the gaseous stream may have more homogeneous composition, simplifying its treatment. The hydroprocessing, as used in the present disclosure, may encompass for example hydrotreatment and/or hydrocracking. By catalytic cracking is meant herein conversion processes encompassing catalytic cracking not consuming added hydrogen, such as fluid catalytic cracking (FCC) or catalytic pyrolysis, and by thermal cracking is meant
30 herein conversion processes based on elevated temperature in the absence of catalyst, such as (non-catalytic) pyrolysis.

In certain preferred embodiments, the refining includes catalytic hydroprocessing, as in catalytic hydroprocessing, such as catalytic hydrotreatment and/or catalytic hydrocracking, the heteroatom cleavage may be more efficient and selective, and upon cleavage e.g.

5 sulphur forms rather H₂S than other sulphur compounds. In certain particularly preferred embodiments, the refining includes catalytic hydroprocessing comprising catalytic hydrotreatment, as utilising catalytic hydrotreatment rather than dedicated catalytic hydrocracking, may help to reduce formation of C₁-C₂ gases, that are generally regarded as lower value products e.g. compared to liquid hydrocarbons, and thereby to improve yield of conversion products having longer carbon chains. Also conversion effluents from catalytic hydrotreatment may have elevated C₃ contents, when the refinery feed comprises fatty materials containing glycerol-backbone in their structure.

10 By hydrotreatment is meant herein a process of treating organic material by means of molecular hydrogen in the presence of a hydrotreatment catalyst. The hydrotreatment reactions may include removal of oxygen from oxygenated hydrocarbons as water i.e. hydrodeoxygenation (HDO), sulphur from organic sulphur compounds as dihydrogen sulphide (H₂S), i.e. hydrodesulphurisation, (HDS), nitrogen from organic nitrogen compounds as ammonia (NH₃), i.e. hydrodenitrogenation (HDN), halogens, for example 15 chlorine from organic chloride compounds as hydrochloric acid (HCl), i.e. hydrodechlorination (HDCI), and/or metals by hydrodemetallization; and/or hydrogenation of olefinic bonds to saturated bonds and/or of aromatics to naphthenes. Depending e.g. on the composition of the feed fed to the hydrotreatment, different reactions may occur and/or prevail in the hydrotreatment. Hydrotreatment is capable of converting hydrotreatment feeds of varying compositions to more pure materials, by reducing content of heteroatoms, metals, 20 olefins, aromatics and/or other less desired compounds in the hydrotreatment feed. Hydrotreatment may also involve certain side reactions, such as hydrocracking reactions.

By hydrocracking is meant herein a catalytic process of treating organic material in the presence of molecular hydrogen, causing the feed molecules to crack into smaller, lower-boiling compounds. The presence of hydrogen ensures reduced olefin formation. 25 Hydrocracking may also involve ring-opening of cyclic feed components, as well as cleavage of heteroatoms. Depending on the feed composition, hydrocracking conditions and the used catalyst, isomerisation reactions may also occur during hydrocracking. Unlike for hydrotreatment catalysts, at least some acidity is required for a hydrocracking catalyst, 30 which may be attained e.g. by using acidic materials and/or incorporating promoters such as certain metals, as is well known in the art.

In exemplary embodiments, the refining includes catalytic hydroprocessing comprising catalytic hydrotreatment, wherein the hydrotreatment is conducted at a temperature within a range from 250 °C to 500 °C, preferably from 300 °C to 450 °C, a pressure within a range

from 1 MPa to 20 MPa, preferably from 5 MPa to 18 MPa, a H₂ partial pressure at the inlet of the hydrotreatment reactor within a range from 1 MPa to 20 MPa, preferably from 5 MPa to 18 MPa, a weight hourly space velocity within a range from 0.1 to 10, preferably from 0.2 to 8 kg refinery feed per kg hydrotreatment catalyst per hour, and a H₂ to refinery feed ratio within a range from 50 to 2000, preferably from 100 to 1500 normal liters H₂ per liter refinery feed, in the presence of a hydrotreatment catalyst. Within these conditions the efficiency of the hydrotreatment step in terms of selectivity and/or activity regarding hydrotreatment reactions, including heteroatom content reduction, olefins saturation and dearomatization, may be further enhanced, hydrotreatment catalyst deactivation controlled, and undesired side reactions suppressed. For example, a relatively high hydrogen pressure in the hydrotreatment may help to minimise presence and formation of olefins, thereby contributing i.a. to improved stability of the degassed hydrocarbon stream and products recovered therefrom. The hydrotreatment catalyst may be any conventionally used hydrotreatment catalyst or combination thereof. Typical hydrotreatment catalyst may comprise at least one or more metals from Group VIII of the Periodic Table and/or from Group VIB of the Periodic Table, preferably at least one or more of Ni, Mo, W, and/or Co, such as NiMo, CoMo, NiCoMo, NiW, and/or NiMoW, preferably on a support such as alumina.

In exemplary embodiments, the refining includes catalytic hydroprocessing comprising catalytic hydrocracking, wherein the hydrocracking is conducted at a temperature within a range from 280 °C to 450 °C, preferably from 300 °C to 420 °C, a pressure within a range from 8 MPa to 20 MPa, preferably from 12 MPa to 18 MPa, a H₂ partial pressure at the inlet of the hydrocracking reactor within a range from 8 MPa to 20 MPa, preferably from 12 MPa to 18 MPa, a weight hourly space velocity within a range from 0.1 to 10, preferably from 0.2 to 8 kg refinery feed per kg hydrocracking catalyst per hour, and a H₂ to refinery feed ratio within a range from 50 to 2000, preferably from 500 to 1500 normal liters H₂ per liter refinery feed, in the presence of a hydrocracking catalyst. Within these conditions the efficiency of the hydrocracking step in terms of selectivity and/or activity regarding hydrocracking reactions may be further enhanced, sufficient heteroatom removal attained, hydrocracking catalyst deactivation controlled, undesired side reactions suppressed and desired conversion level reached. For example, a relatively high hydrogen pressure in the hydrocracking may help to minimise presence and formation of olefins, thereby contributing i.a. to improved stability of the degassed hydrocarbon stream and products recovered therefrom. The hydrocracking catalyst may be any conventionally used hydrocracking catalyst or combination thereof. Typically, the hydrocracking catalyst is a bifunctional

hydrocracking catalyst comprising at least one or more metal, and at least one or more acidic porous material.

In the present process and system, the conversion effluent is subjected to separation in a separation section to obtain a gaseous stream comprising H₂S and at least one or more of carbon oxide(s) and/or C1-C3 hydrocarbons, and a degassed hydrocarbon stream. Typically, the separation is conducted in several steps in the separation section. Although herein referred to as singular, in practice several gaseous streams comprising H₂S and at least one or more of carbon oxide(s) and/or C1-C3 hydrocarbons may be obtained in the separation section, some of which may be combined before subjecting to sweetening. Preferably biogenic carbon content in each of such gaseous streams is determined in the present process and system. In the separation, water that may form during the refining in the conversion unit e.g. in the course of deoxygenation of oxygenated hydrocarbons, is typically also separated and removed. The separation may be referred to as a gas-liquid separation as the separation allows recovery of compounds that are gaseous under the separation conditions. The initial gas-liquid separation may be conducted for example as an integral step within the conversion unit, such as in the (last) conversion reactor of the conversion unit, although usually as a separate step. Typically, the separation steps are conducted at different temperatures within a range from 0 °C to 500 °C, such as from 15°C to 300°C. Preferably at least the initial gas-liquid separation step is conducted at essentially same pressure as that of the (last) reactor in the conversion unit wherefrom the effluent originates. Typically, the pressure during the separation steps may be within a range from 0.1 MPa to 20 MPa, such as from 1 MPa to 18 MPa. In certain preferred embodiments, the conversion effluent is subjected to the separation utilising at least one or more of high pressure high temperature separator(s), high pressure low temperature separator(s), high pressure medium temperature separator(s), low pressure high temperature separator(s), low pressure medium temperature separator(s), low pressure low temperature separator(s), stripper(s), gas scrubber(s), gas knock out drum(s), horizontal separator(s), vertical separator(s), three-phase separator(s), cyclone separator(s), centrifugal separator(s), and/or gunbarrel tank(s), to obtain the gaseous stream comprising H₂S and at least one or more of carbon oxide(s) and/or C1-C3 hydrocarbons.

In addition to an initial gas-liquid separation, in certain preferred embodiments the separation in step c) may further include removing from the gaseous stream at least part of hydrocarbons having 8 or more carbon atoms, preferably at least part of hydrocarbons having 7 or more carbon atoms, more preferably at least part of hydrocarbons having 6 or more carbon atoms, even more preferably at least part of hydrocarbons having 5 or more

carbon atoms, as may be entrained in the gaseous stream, before collecting an aliquot of the gaseous stream as a sample. This may be attained for example by condensating the gaseous stream e.g. using high pressure and/or lowered temperature, and distilling and/or flashing the condensate, or by using centrifugal separation, or by any other conventionally used methods. For example, the reactor effluent may be subjected to initial gas-liquid separation in a high pressure medium temperature separator to obtain a liquid intermediate stream and a gaseous stream, and subjecting the latter to separation in a high pressure low temperature separator to remove condensed hydrocarbons. By including in the separation section removal of at least part of the heaviest hydrocarbons that may be present in the gaseous stream(s), valuable further liquid intermediate stream(s) may be obtained usable e.g. as a gasoline fuel component and/or as a co-feed to a hydrogen production unit such as steam reforming, to obtain a syngas, followed by recovering a make-up hydrogen stream from the syngas. The biogenic carbon content in such further liquid intermediate stream(s) may be determined using conventional methods, preferably using AMS technique. Alternatively, the liquid intermediate stream(s) obtained in the separation section may be combined to obtain the degassed hydrocarbon stream, optionally after subjecting to further separation e.g. in a stripper, where also the unstabilised naphtha stream may be separated.

In addition to H₂S, carbon oxide(s) and C₁-C₃ hydrocarbons, exemplary compounds that may also be retained in the gaseous stream separated from the conversion effluent include at least one or more of hydrogen and/or ammonia. Particularly when the refining is hydroprocessing, the conversion effluent may be rich in residual hydrogen.

In the present process and system for producing hydrocarbons having biogenic carbon content the separated gaseous stream is subjected to a sweetening treatment to obtain a sweetened gas stream. In certain preferred embodiments, the sweetening treatment comprises at least absorption. Sweetening treatment involving absorption is preferred as absorption into liquid solvent(s) is cost-efficient, very commonly used in refineries for acid gas removal, various liquid solvent absorbents exist, as well as efficient regeneration procedures for them. When the sweetening treatment comprises absorption, the absorption may be conducted using any suitable liquid absorbents including common physical solvents such as methanol (e.g. Rectisol), dialkyl ethers of polyethylene glycol (e.g. Selexol), sulfolane, N-methyl-2-pyrrolidone (e.g. Purisol), propylene carbonate (e.g. Fluor Solvent), morpholine derivatives (e.g. Morphysorb); alkanolamines including primary amines such as monoethanolamine (MEA), diglycolamine (DGA) or 2-amino-2-methyl-1-propanol (AMP), secondary amines such as diethanolamine (DEA) or diisopropanolamine (DIPA), tertiary amines such as N-methyldiethanolamine (MDEA) or triethanolamine (TEA); ionic liquids

that are liquids composed of ions; deep eutectic solvents that are multicomponent mixtures of hydrogen bond acceptors and donors; or any combinations thereof, optionally with additives. Various other sweetening treatments are also commonly known, and may be used in the sweetening treatment of the present process and system in addition or instead of absorption. However, in certain particularly preferred embodiments, the sweetening treatment comprises at least absorption using at least one or more of physical solvent(s) and/or alkanolamine(s).

Additionally or alternatively, in certain preferred embodiments the sweetening treatment is conducted in a common sweetening unit receiving the gaseous stream and one or more further gaseous stream(s) separated from further conversion effluent(s) obtained by refining further refinery feed(s) in further conversion unit(s). Utilising a common sweetening unit provides the further benefits of decreasing investment and operating costs.

In certain preferred embodiments, before (i.e. upstream of) the gaseous stream is subjected to the sweetening treatment, but after (i.e. downstream of) the aliquot of the gaseous stream is collected, the gaseous stream is combined with one or more further gaseous stream(s) separated from further conversion effluent(s) obtained by refining further refinery feed(s) in further conversion unit(s), wherein the further gaseous stream(s) optionally has/have lower biogenic carbon content than the gaseous stream or essentially no biogenic carbon content, and the gaseous stream is subjected to the sweetening treatment in step d) as combined with said further gaseous stream(s). The further conversion effluent(s) may be obtained by refining further refinery feed(s) in further conversion unit(s), wherein the refining in the further conversion unit(s) may be selected from further catalytic hydroprocessing, further catalytic cracking, and further thermal cracking, preferably from further catalytic hydroprocessing, more preferably from further catalytic hydroprocessing comprising further catalytic hydrotreatment, for similar reasons as discussed in connection with the refining in the conversion unit of step b). The further gaseous stream(s) separated from further conversion effluent(s) may contain similar compounds as the gaseous stream separated in step c) i.e. at least one or more of H₂S, carbon oxide(s), C₁-C₃ hydrocarbons, hydrogen, and/or ammonia. Utilising a common sweetening unit provides the further benefits of decreasing investment and operating costs, but combining the gaseous stream having biogenic carbon content with further gaseous stream(s) having lower or no biogenic carbon content may dilute the biogenic carbon content of the gaseous stream below the detection limit of the biogenic carbon content determination, hence underlining the advantages of the present process and systems.

The sweetened gas stream may be subjected to typical refinery gas treatments, depending on the composition of the gaseous stream. In certain preferred embodiments, the sweetened gas stream is subjected at least to hydrogen recovery in a hydrogen recovery unit to obtain a recycle hydrogen stream, and to recovery of a gas stream containing C1-C3 hydrocarbons, and at least a portion of the gas stream containing C1-C3 hydrocarbons, and optionally C5-C8 hydrocarbons removed from the gaseous stream in step c), is/are fed to a hydrogen production unit, preferably to a steam reforming unit, to obtain a syngas, followed by recovering a make-up hydrogen stream from the syngas. In preferred further embodiments, the refining in step b) comprises catalytic hydroprocessing, and at least a portion of the recovered recycle hydrogen stream and/or of the recovered make-up hydrogen stream is fed to the catalytic hydroprocessing. These embodiments provide further enhancement of the process economy and sustainability.

The present process and system involve e1) collecting an aliquot of the gaseous stream as a sample before (i.e. upstream of) subjecting the gaseous stream to the sweetening treatment; e2) subjecting the sample to a selective H₂S removal treatment to obtain a selectively H₂S depleted sample; e3) optionally subjecting the selectively H₂S depleted sample to drying to obtain a dehydrated sample; and e4) subjecting the selectively H₂S depleted and optionally dehydrated sample to a biogenic carbon content determination, preferably using accelerator mass spectrometry (AMS) technique, to obtain the content of biogenic carbon in the gaseous stream.

WO2021100004A1 teaches that due to long analysis times, instrument cost, and tedious sample preparation methods, AMS technique, and ASTM standard D6866 methods, would be unsuitable for implementing the technique in a refinery. However, the present inventors have found that steps e1) to e4) of the present process/system and/or the present sample treatment and analysis system provide not only safe but also convenient i.e. sufficiently robust way to determine biogenic carbon content also in the gaseous output stream comprising H₂S and at least one or more of carbon oxide(s) and/or C1-C3 hydrocarbons, of a refinery conversion unit, even when utilising a biogenic carbon content analyzer using AMS technique.

The sequence of steps e1) to e4) does not need to be conducted continuously during the running of the present process or when using the present system. Preferably the sequence of steps e1) to e4) is conducted intermittently, i.e. from time to time or as campaigns, preferably on a need basis such as when changes in the composition of the separated gaseous stream(s) and in the optionally separated unstabilised naphtha stream are

foreseen. Continuous analysis may be difficult to arrange particularly for the unstabilised naphtha sample. Since conducting the sequence of steps e1) to e4) is initiated by collecting an aliquot of the gaseous stream as a sample, in certain preferred embodiments, in step e1) the aliquots of the unstabilised naphtha stream are collected intermittently. Preferably also the aliquots of the gaseous stream are collected intermittently. Examples of situations where changes in the composition of the separated gaseous stream(s) and in the optionally separated unstabilised naphtha stream are foreseen include changes in the composition of the refinery feed, changes in the operating conditions of the conversion unit, changes in the activity and/or selectivity of a catalyst optionally used in the refining in the conversion unit, and/or changes in the operating conditions of the separation section. When the sequence of steps e1) to e4) is conducted intermittently during the running of the present process/system, the steps e1) to e4), particularly collecting of the aliquots of the gaseous stream, or collecting of the aliquots of the optionally separated unstabilised naphtha stream, may be conducted periodically i.e. approximately within fixed intervals or occasionally i.e. within varying intervals. In certain embodiments, the sequence of steps e1) to e4), particularly collecting of the aliquots of the gaseous stream and/or collecting of the aliquots of the optionally separated unstabilised naphtha stream, to obtain the content of biogenic carbon in the gaseous stream or in the unstabilised naphtha stream, respectively, may be conducted more frequently when taking the present process/system in use. The present process/system may also involve creating a database containing information on the obtained content of biogenic carbon in the gaseous stream and/or in the optionally separated unstabilised naphtha stream, as well as the respective refinery feed composition, operating conditions in the conversion unit, selectivity and/or activity and/or time-on-stream of an optionally used catalyst, and/or operating conditions in the separation section at the time; using the database for creating and/or training a model for estimating the biogenic carbon content in the gaseous stream and/or in the optionally separated unstabilised naphtha stream; and at times when not conducting the sequence of steps e1) to e4), using the model for obtaining the biogenic carbon content in the gaseous stream and/or or in the optionally separated unstabilised naphtha stream. In these embodiments of the present process/system, the sequence of steps e1) to e4), particularly collecting of the aliquots of the gaseous stream and/or collecting of the aliquots of the optionally separated unstabilised naphtha stream, may be conducted from time to time to revalidate or calibrate the model. The benefits of collecting the aliquots of the gaseous stream or the aliquots of the optionally separated unstabilised naphtha stream intermittently include reduced risk of exposure of personnel to H₂S, and reduced costs of operating steps e1) to e4) as well as possibility to use the same sample treatment and analysis system in determining biogenic carbon content

in multiple separated gaseous streams and in the unstabilised naphtha stream, one at a time. In certain embodiments, the aliquots of the gaseous stream(s) or the aliquots of the optionally separated unstabilised naphtha stream are collected in the separation section or thereafter, preferably from a separator, vessel or pipeline having low pressure.

- 5 The collected sample, whether originating from the gaseous stream or from the unstabilised naphtha stream, is then subjected to selective H₂S removal treatment. This is conducted in order to enhance safety of the biogenic carbon content determination. Furthermore, H₂S may interfere with the sample preparation and/or biogenic carbon content determination, especially when using accelerator mass spectrometry (AMS) technique. More specifically,
- 10 H₂S may negatively influence reduction of CO₂ to graphite that may be conducted in the sample preparation for biogenic carbon content measurement by AMS technique, even leading to an erroneous result. The selective H₂S removal treatment step/unit of the present process/system may utilise any sufficiently selective H₂S removal treatment known in the field. In certain preferred embodiments, the selective H₂S removal treatment comprises at
- 15 least adsorption, i.e. use of solid adsorbent(s). As is well known to a skilled person, chemisorption is associated with covalent and/or hydrogen bonding interactions, while physisorption is associated with Van der Waals forces and/or electrostatic interactions. It is to be understood that even when adsorption involves predominantly e.g. chemisorption, physisorption may also occur to some extent. In certain particularly preferred embodiments,
- 20 in step e2) the selective H₂S removal treatment comprises adsorption, preferably adsorption predominantly based on chemisorption. The present inventors found that chemisorption may provide better selectivity towards H₂S, reaching very low residual H₂S content in the sample, typically at most 200 w-ppm of H₂S, based on the total weight of the sample, and that adsorption predominantly based on chemisorption may help to maintain
- 25 the sample composition otherwise essentially unchanged. The predominance of chemisorption over physisorption may be contributed e.g. by suitable adsorbent selection. In certain preferred embodiments of the present process and systems, the selective H₂S removal treatment comprises adsorption on at least one or more metal oxide(s), preferably at least one or more selected from oxides of Fe, Mn, Zn, Cu, Co, Mo, and/or Ca. Metal
- 30 oxides have typically high chemical affinity for H₂S, and they are commonly available. The metal oxide(s) capture H₂S predominantly by chemisorption, resulting in formation of sulphides, elemental sulphur and/or sulphates. Metal oxides may provide higher adsorption capacities at a lower material price compared e.g. to zeolites. More preferably the selective H₂S removal treatment comprises adsorption on at least one or more metal oxide(s)
- 35 selected from oxides of Fe, Mn, Zn, Cu, and/or Co, as these may have high chemical affinity

for H₂S even at lower temperatures. As specific examples of preferred adsorbents one may mention e.g. adsorbents containing KMnO₄ and alumina, such as Chemisorb® P, and adsorbents containing Fe(III) oxide, such as Sulfurtrap® ST1.

Optionally, the present process and systems may involve subjecting the selectively H₂S
5 depleted sample to drying to obtain a dehydrated sample. Some water may be formed in
the selective H₂S removal treatment, particularly when this treatment involves
chemisorption. The dehydration may be particularly beneficial, when it is desired to verify
the composition of the sample by gas chromatography (GC), for which the presence of
10 water/moisture may be harmful. Inorganic salts are known for their usability for water
removal. However, their reactions with water are exothermic. Hence, in certain preferred
embodiments, the optional drying is based on dehydration using at least one or more
synthetic polymers, preferably synthetic ionomers (i.e. synthetic polymers with ionic
properties), more preferably sulfonated tetrafluoroethylene based fluoropolymer-
15 copolymers, such as Nafion incorporating perfluorovinyl ether groups terminated with
sulfonate groups onto a tetrafluoroethylene (PTFE) backbone. Synthetic polymers are not
consumed in the cause of dehydration, and no reagent replacements are needed. Further
preferably, the present process/systems may involve subjecting a portion of the selectively
H₂S depleted and preferably dehydrated sample to a composition analysis using GC, e.g.
20 to verify successful removal of H₂S, and that the composition of the gaseous stream
remains otherwise unchanged.

Thereafter, the present process/systems involves subjecting the selectively H₂S depleted
and optionally dehydrated sample, or a portion thereof, to a biogenic carbon content
determination, preferably using accelerator mass spectrometry (AMS) technique, to obtain
the content of biogenic carbon in the gaseous stream. AMS is preferred due to its
25 preciseness, even for gaseous samples. As used herein, the biogenic carbon content
determination or analyzer, whether using AMS or another technique, is to be understood as
including the usual sample preparation steps that are well known for the selected technique.
For example, the sample preparation for AMS technique may involve oxidation of all carbon
present in the sample to CO₂ and reduction of the CO₂ to graphite. As the results are
30 presented as the biogenic carbon mass percentage of the total carbon of the sample,
removal of H₂S, H₂O or other non-carbon containing component from the gaseous stream
holds no significance to the biogenic carbon content in the gaseous stream, and
consequently removal of non-carbon containing compounds does not require e.g. any
corrective calculations.

In certain preferred embodiments, in step f) at least one or more distillate(s) and a fractionation bottom are further separated from the degassed hydrocarbon stream, and the biogenic carbon content in all the recovered distillate(s) and in the fractionation bottom are determined, preferably using AMS technique. The separation to obtain the distillate(s) and the bottom may comprise for example steam stripping and/or distillation, or any other technology conventionally used in fractionation sections.

According to a second example aspect a system for producing hydrocarbons having biogenic carbon content is provided, the system comprising:

- a) at least one or more refinery feed tank(s) configured to receive a refinery feed having biogenic carbon content, non-biogenic carbon content and sulphur content, or components of the refinery feed;
- b) a conversion unit in fluid communication with the refinery feed tank(s), and configured to receive and refine the refinery feed to obtain a conversion effluent comprising at least H₂S and hydrocarbons, and preferably also carbon oxide(s);
- c) a separation section in fluid communication with the conversion unit and configured to receive the conversion effluent and to separate therefrom a gaseous stream comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons, and a degassed hydrocarbon stream, and optionally an unstabilised naphtha stream comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons, wherein the separation section is optionally further configured to separate from the degassed hydrocarbon stream at least one or more distillate(s) and a fractionation bottom;
- d) a sweetening unit in fluid communication with the separation section and configured to receive and sweeten the gaseous stream to obtain a sweetened gas stream; and
- e) a sample treatment and analysis system comprising:
 - e1) a sampler in communication, preferably in fluid communication, with the separation section and configured to collect as a sample an aliquot of the gaseous stream as a sample at a location upstream of the sweetening unit,
 - e2) a selective H₂S removal unit in communication, preferably in fluid communication, with the sampler and configured to receive the sample and to selectively remove H₂S from the sample to obtain a selectively H₂S depleted sample,
 - e3) an optional drying unit in communication, preferably in fluid communication, with the selective H₂S removal unit and configured to receive and dehydrate the selectively H₂S depleted sample to obtain a dehydrated sample, and an optional gas

chromatography (GC) analyzer in communication, preferably in fluid communication, with the selective H₂S removal unit optionally via the drying unit and configured to receive a portion of the selectively H₂S depleted and optionally dehydrated sample, and

- 5 e4) a biogenic carbon content analyzer, preferably using accelerator mass spectrometry (AMS) technique, in communication, preferably in fluid communication, with the selective H₂S removal unit optionally via the drying unit, and configured to receive at least a portion of the selectively H₂S depleted and optionally dehydrated sample and to determine its biogenic carbon content to obtain the content of biogenic
10 carbon in the gaseous stream.

According to a third example aspect a sample treatment and analysis system is provided, the system comprising:

- e1) a sampler configured to collect a sample comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons,
- 15 e2) a selective H₂S removal unit in communication, preferably in fluid communication, with the sampler and configured to receive the sample and to selectively remove H₂S from the sample to obtain a selectively H₂S depleted sample,
- e3) an optional drying unit in communication, preferably in fluid communication, with the selective H₂S removal unit and configured to receive and dehydrate the selectively H₂S
20 depleted sample to obtain a dehydrated sample, and an optional gas chromatography (GC) analyzer in communication, preferably in fluid communication, with the selective H₂S removal unit optionally via the drying unit and configured to receive a portion of the selectively H₂S depleted and optionally dehydrated sample, and
- e4) a biogenic carbon content analyzer, preferably using accelerator mass spectrometry
25 (AMS) technique, in communication, preferably in fluid communication, with the selective H₂S removal unit optionally via the drying unit, and configured to receive at least a portion of the selectively H₂S depleted and optionally dehydrated sample and to determine its biogenic carbon content to obtain the content of biogenic carbon in the collected sample.

- In certain preferred embodiments of the sample treatment and analysis system, the
30 collected sample is an aliquot of a gaseous stream comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons; or

the collected sample is an aliquot of an unstabilised naphtha stream comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons, and the sample treatment and analysis system further comprises:

- 5 i) a phase separator in communication, preferably in fluid communication, with the sampler and configured to receive the sample and to subject it to phase separation to obtain a gas-phase sample and a liquid naphtha sample, and to pass the gas-phase sample to the selective H₂S removal unit of e2) to obtain in e4) the content of biogenic carbon in the gas-phase sample and to pass the liquid naphtha sample to a biogenic carbon content analyzer to determine its biogenic carbon content to obtain the content of biogenic carbon in the liquid naphtha sample, allowing calculation of the biogenic carbon content in the collected sample based on the contents of biogenic carbon in the gas-phase sample and in the liquid naphtha sample; or
- 10 ii) a high-pressure compressor in communication, preferably in fluid communication, with the sampler and configured to receive and compress the collected sample to obtain a liquefied sample, and to pass the liquefied sample to the selective H₂S removal unit of e2), wherein the system is configured to maintain the liquefied sample in the liquefied state until fed to the biogenic carbon content analyzer of e4).
- 15

It should be appreciated that while the units utilised in steps e1) to e4) are preferably arranged in fluid communication, at least some of them may be arranged in communication requiring e.g. manual input. For example, the sample may be delivered to the selective H₂S removal unit manually, and/or the at least a portion of the selectively H₂S depleted and optionally dehydrated sample may be delivered to the biogenic carbon content analyzer manually, just to name a few examples where other than fluid communication may be utilised. Particularly when the aliquots of the gaseous stream are collected intermittently, e.g. with long intervals, arranging at least some of the communications manually may even be preferred, as not requiring investment in the connecting hardware. Furthermore, the communication is not necessarily direct but may be arranged indirectly such as via another unit. For example, the biogenic carbon content analyzer may be in communication with the selective H₂S removal unit via an optional drying unit.

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30 According to a fourth example aspect there is provided use of the system for producing hydrocarbons having biogenic carbon content according to the second example aspect, or of the sample treatment and analysis system according to the third example aspect, in a process for producing hydrocarbons having biogenic and non-biogenic carbon content, preferably in a process according to the first example aspect.

According to a fifth example aspect there is provided use of the sample treatment and analysis system according to the third example aspect for creating and/or training a model for estimating biogenic carbon content of a gaseous stream and/or of an unstabilised naphtha stream in a process for producing hydrocarbons having biogenic carbon content, wherein the gaseous stream and the unstabilised naphtha stream comprise H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons and are obtainable by separating from a conversion effluent obtained by refining in a conversion unit a refinery feed having biogenic carbon content, non-biogenic carbon content and sulphur content; preferably for creating and/or training a model for estimating biogenic carbon content of a gaseous stream and/or of an unstabilised naphtha stream in a process according to the first example aspect. Such a model may be created and/or trained for example based on a database as explained in the foregoing.

In embodiments of the system according to the second example aspect, any one or more of the refinery feed, the refinery feed components, the conversion unit, the conversion effluent, the separation or separation section, the gaseous stream comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons, the degassed hydrocarbon stream, the sweetening treatment or unit, the sweetened gas stream, the sample treatment and analysis system, the sampler, the sample, the selective H₂S removal treatment or unit, the selectively H₂S depleted sample, the drying or drying unit, the dehydrated sample, the biogenic carbon content determination or analyzer, the at least one or more distillate(s), and/or the fractionation bottom, may be as specified in the present disclosure in connection with the embodiments of the process according to the first example aspect and/or in connection with the embodiments of the sample treatment and analysis system according to the third example aspect. Similarly, in embodiments of the sample treatment and analysis system according to the third example aspect, any one or more of the sampler, the gaseous stream comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons, the sample, the selective H₂S removal treatment or unit, the selectively H₂S depleted sample, the drying or drying unit, the dehydrated sample, the biogenic carbon content determination or analyzer, and/or the dehydrated sample, may be as specified in the present disclosure in connection with the embodiments of the process according to the first example aspect and/or as specified in the present disclosure in connection with the embodiments of the system according to the second example aspect. Further similarly, in embodiments of the use according to the fourth example aspect or the fifth example aspect, the process for producing hydrocarbons having biogenic carbon content, or any steps or features of the process, may be as specified in the present

disclosure in connection with the embodiments of the process according to the first example aspect.

Schematic presentation of the process and the systems

Fig. 1 schematically shows a sample treatment and analysis system according to an example embodiment. Fig 1 shows a sampler 300 configured to collect an aliquot of a gaseous stream 30 comprising H₂S and at least one or more of carbon oxide(s) and/or C1-C3 hydrocarbons as a sample 200, and a selective H₂S removal unit 310 in communication with the sampler 300 and configured to receive the sample 200 and to selectively remove H₂S from the sample to obtain a selectively H₂S depleted sample 210. An optional drying unit 320 may be arranged in communication with the selective H₂S removal unit 310 and configured to receive and dehydrate the selectively H₂S depleted sample 210 to obtain a dehydrated sample 220. A biogenic carbon content analyzer 330, preferably using accelerator mass spectrometry (AMS) technique, is arranged in communication with the selective H₂S removal unit 310, optionally via the drying unit 320, and configured to receive at least a portion of the selectively H₂S depleted sample 210, or the selectively H₂S depleted and dehydrated sample 220, and to determine its biogenic carbon content. Based on the output value of the biogenic carbon content analyzer 330, the content of biogenic carbon in the gaseous stream 30, as a wt.-% based on the total weight of carbon (TC) in the gaseous stream, is obtained. Additionally, the sample treatment and analysis system may comprise an optional gas chromatography (GC) analyzer (not shown in Figure 1) arranged in communication with the selective H₂S removal unit 310, optionally via the drying unit 320, and configured to receive a portion of the selectively H₂S depleted sample 210, or the selectively H₂S depleted and dehydrated sample 220, to be subjected to a composition analysis. The sample treatment and analysis system may be modified to facilitate determination of biogenic carbon content in unstabilised naphtha. In such configurations, e.g. a phase separator or a high-pressure compressor (not shown in Fig 1) may be arranged downstream of and in communication with the sampler 300, as explained in the foregoing.

Fig. 2 schematically shows a process and a system for producing hydrocarbons having biogenic carbon content, according to an example embodiment. Fig. 2 shows at least one or more refinery feed tank(s) 100, 110 configured to receive a refinery feed having biogenic carbon content, non-biogenic carbon content and sulphur content 10, or components thereof. The refinery feed having biogenic carbon content, non-biogenic carbon content and sulphur content 10 is refined in a conversion unit 120 to obtain a conversion effluent 20

comprising at least H₂S and hydrocarbons, and preferably carbon oxide(s). The conversion effluent 20 is then subjected to a separation in a separation section 130 to obtain a gaseous stream 30 comprising H₂S and at least one or more of carbon oxide(s) and/or C1-C3 hydrocarbons, and a degassed hydrocarbon stream 400. Optionally also an unstabilised naphtha stream (not shown in Fig 2) may be separated in the separation section. The degassed hydrocarbon stream 400 may be utilised as such, or optionally introduced into a further separation for example using a distillation column 140 so as to separate from the degassed hydrocarbon stream 400 at least one or more distillate(s) 410, 420, and a fractionation bottom 430. The gaseous stream 30 is subjected to a sweetening treatment in a sweetening unit 150 to remove sour gases 60, such as H₂S and CO₂, and to obtain a sweetened gas stream 70. The gaseous stream 30 may be subjected to the sweetening treatment alone, or as combined with one or more further gaseous stream(s) 40, 50 separated from further conversion effluent(s) obtained by refining further refinery feed(s) in further conversion unit(s). Optionally the sweetened gas stream 70 may be subjected to hydrogen recovery in a hydrogen recovery unit 160 to obtain a recycle hydrogen stream 80 and a gas stream containing C1-C3 hydrocarbons 90. Before (i.e. upstream of) subjecting the gaseous stream 30 to the sweetening treatment, and preferably before (i.e. upstream of) optional combining of further gaseous streams 40, 50, an aliquot of the gaseous stream 30 is collected as a sample 200 with a sampler 300, and processed as explained above in connection with Fig. 1, preferably using the sample treatment and analysis system according to Fig. 1.

EXAMPLES

Example 1. Selectivity tests of the H₂S removal treatment

In the selectivity tests a gaseous stream from a refinery conversion unit fed with a 100% petroleum feed was utilised, hence not containing carbon oxides. This example illustrates the efficiency and selectivity of the H₂S removal treatment of the present sample treatment and analysis system.

An aliquot of the gaseous stream was collected at a location upstream of a sweetening unit and before combining with any other gaseous streams. The aliquot was split to provide two parallel samples. One of the parallel samples was used for determining composition of the gaseous stream using gas chromatography, following extreme care and safety precautions due to H₂S present in the sample. The composition is presented in Table 1.

The other parallel sample was subjected to a selective H₂S removal treatment by passing the sample through a column packed with Sulfurtrap® ST1 granules, containing Fe(III) oxide absorbent, to obtain a selectively H₂S depleted sample, which was further passed through a Nafion® tube to obtain a selectively H₂S depleted and dehydrated sample. A portion of the selectively H₂S depleted and dehydrated sample was then used for determining composition of this treated sample with gas chromatography (GC). Also these results are presented in Table 1.

Table 1. Concentration of components in the sample before and after selective H₂S removal treatment with Sulfurtrap® ST1 and drying.

Component	Concentration before (mol-%)	Concentration after (mol-%)
Methane	9.2	8.7
C2 and C3 hydrocarbons	12.1	13.2
C4 hydrocarbons	7.0	7.7
C5 hydrocarbons	3.7	3.5
H ₂	62.8	61.8
CO ₂	0.0	0.0
H ₂ S	3.6	0.0
CO	0.0	0.0

As can be seen from Table 1, the selective H₂S removal was efficient and removed H₂S essentially completely. At the same time the levels of H₂ and C1-C5 hydrocarbons remained essentially unchanged, verifying that the H₂S removal was sufficiently selective.

Another test was conducted using a similarly collected aliquot of a refinery unit gaseous stream and procedure as above, but this time subjecting one parallel sample to a selective H₂S removal treatment by passing the sample through a column packed with Chemisorb® P granules containing KMnO₄ and alumina, to obtain a selectively H₂S depleted sample, which was further passed through a Nafion® tube to obtain a selectively H₂S depleted and dehydrated sample. The other parallel sample was used for determining composition of the gaseous stream using gas chromatography. The results of these tests are presented in Table 2.

Table 2. Concentration of components in the sample before and after selective H₂S removal treatment with Chemisorb® P and drying.

Component	Concentration before (mol-%)	Concentration after (mol-%)
Methane	7.8	7.9
C2 and C3 hydrocarbons	15.1	14.3

C4 hydrocarbons	10.5	10.2
C5 hydrocarbons	5.6	5.9
H ₂	53.1	54.7
CO ₂	0.0	0.0
H ₂ S	5.2	0.0
CO	0.0	0.0

As can be seen from Table 2, the selective H₂S removal was efficient and removed H₂S essentially completely also with this adsorbent. At the same time levels of H₂ and C1-C5 hydrocarbons remained essentially unchanged, verifying that the H₂S removal was sufficiently selective also with this adsorbent.

5 Example 2. Biogenic carbon contents of output streams and mass-balance of a conversion unit

A refinery feed comprising 10 wt.-% of a mixture of conventionally purified animal fats and vegetable oils and 90 wt.-% of a petroleum feed containing 0.8 wt.-% of sulphur (ASTM D7039-15a(2020)) was subjected to hydrotreatment in a hydrotreatment reactor in the presence of a conventional hydrotreatment catalyst containing sulphided NiMo on alumina. The hydrotreatment effluent was subjected to a separation using a high-pressure medium-temperature separator to obtain a gaseous stream and a degassed hydrocarbon stream. The degassed hydrocarbon stream was fed to a fractionation section to recover distillates as well as a fractionation section bottom. Biogenic carbon content in each output stream were determined and are presented in Table 3. The separated gaseous stream was subjected to a sweetening treatment in an amine scrubber unit together with gaseous streams from other conversion units to obtain H₂S and CO₂ depleted (sweetened) gas stream.

An aliquot of the gaseous stream was collected as a sample at a location upstream of the sweetening unit and before combining with other gaseous streams. The sample was subjected to a selective H₂S removal treatment and dehydration as described in Example 1. The selectively H₂S depleted and dehydrated sample was subjected to a biogenic carbon content determination, using accelerator mass spectrometry (AMS) analyzer, to obtain the content of biogenic carbon in the sample, representing the gaseous stream. The obtained value is reported in Table 3.

Table 3. Example of biogenic carbon content of a gaseous stream, distillates and fractionation bottom, as well as mass-balance of an exemplary conversion unit, with a biogenic feed of 10 wt.-% in total refinery feed.

Output stream of a conversion unit	Biogenic carbon content, wt.-% of total carbon (EN 16640:2017)	Mass-balance (t/h)
Gaseous stream*	~5-10	N/A
Gasoline	0.11	0.03
Kerosene	1.6	0.78
Gas oil	8.77	7.74
Fractionation bottom	0.72	0.17

* Determined as disclosed above

5 As can be seen from Table 3, the gaseous stream from a conversion unit can be substantial and is likely to contain a significant amount of biogenic carbon due to the glycerol backbone of fatty acids being converted into e.g. propane. By using the present process and systems, it is possible to capture the biogenic carbon content of the gaseous stream that would otherwise be lost (remain unknown) completely, or at least in part.

10 Various embodiments have been presented. It should be appreciated that in this document, words comprise, include and contain are each used as open-ended expressions with no intended exclusivity.

The foregoing description has provided by way of non-limiting examples of particular implementations and embodiments of the invention a full and informative description of the best mode presently contemplated by the inventors for carrying out the invention. It is however clear to a person skilled in the art that the invention is not restricted to details of the embodiments presented in the foregoing, but that it can be implemented in other embodiments using equivalent means or in different combinations of embodiments without deviating from the characteristics of the invention.

20 Furthermore, some of the features of the afore-disclosed embodiments of this invention may be used to advantage without the corresponding use of other features. As such, the foregoing description shall be considered as merely illustrative of the principles of the present invention, and not in limitation thereof. Hence, the scope of the invention is only restricted by the appended patent claims.

CLAIMS

1. A process for producing hydrocarbons having biogenic carbon content, the process comprising:
- 5 a) providing a refinery feed having biogenic carbon content, non-biogenic carbon content and sulphur content;
- b) refining the refinery feed in a conversion unit to obtain a conversion effluent comprising at least H₂S and hydrocarbons, and preferably also carbon oxide(s);
- c) subjecting the conversion effluent to separation in a separation section to obtain a gaseous stream comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons, and a degassed hydrocarbon stream;
- 10 d) subjecting the gaseous stream to a sweetening treatment to obtain a sweetened gas stream; and
- e1) collecting an aliquot of the gaseous stream as a sample before subjecting the gaseous stream to the sweetening treatment,
- 15 e2) subjecting the sample to a selective H₂S removal treatment to obtain a selectively H₂S depleted sample,
- e3) optionally subjecting the selectively H₂S depleted sample to drying to obtain a dehydrated sample, and
- e4) subjecting at least a portion of the selectively H₂S depleted and optionally dehydrated sample to a biogenic carbon content determination, preferably using accelerator mass spectrometry (AMS) technique, to obtain the content of biogenic carbon in the gaseous stream; and
- 20 f) optionally further separating from the degassed hydrocarbon stream at least one or more distillate(s), and a fractionation bottom.
- 25 2. The process according to claim 1, wherein the separation in step c) further includes separating an unstabilised naphtha stream comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons, and

wherein the process further comprises collecting an aliquot of the unstabilised naphtha stream as a naphtha sample, and

- 5 i) subjecting the naphtha sample to phase separation to obtain a gas-phase sample and a liquid naphtha sample, subjecting the gas-phase sample to a procedure according to steps e2) to e4) to obtain the content of biogenic carbon in the gas-phase sample, subjecting the liquid naphtha sample to a biogenic carbon content determination, preferably using accelerator mass spectrometry (AMS) technique, to obtain the content of biogenic carbon in the liquid naphtha sample, and calculating the biogenic carbon content in the unstabilised naphtha stream based on the contents of biogenic carbon in the gas-phase sample and in the liquid naphtha sample; or
- 10 ii) subjecting the naphtha sample to high pressure compression to obtain a liquefied sample, and subjecting the liquefied sample to a procedure according to steps e2) to e4) to obtain the content of biogenic carbon in the unstabilised naphtha stream.
- 15 3. The process according to claim 1 or 2, wherein the refinery feed comprises at least one or more of vegetable oil(s), animal fat(s), microbial oil(s), lignocellulose-derived biocrude(s), used lubricating oil(s) having biogenic carbon content, and/or liquefied organic waste having biogenic carbon content, and at least one or more of petroleum feed(s), used lubricating oil(s) having non-biogenic carbon content, and/or liquefied organic waste having non-biogenic carbon content; preferably at least one or more of vegetable oil(s), animal fat(s), microbial oil(s), and/or lignocellulose-derived biocrude(s), and at least one or more petroleum feed(s).
- 20 4. The process according to any one of the preceding claims, wherein in step b) the refining includes at least one or more of catalytic hydroprocessing, catalytic cracking, and/or thermal cracking, preferably at least catalytic hydroprocessing, more preferably catalytic hydroprocessing comprising at least catalytic hydrotreatment.
- 25 5. The process according to any one of the preceding claims, wherein the separation in step c) may further include removing from the gaseous stream at least part of hydrocarbons having 8 or more carbon atoms, preferably at least part of hydrocarbons having 7 or more carbon atoms, more preferably at least part of hydrocarbons having 6 or more carbon atoms, even more preferably at least part of hydrocarbons having 5 or more carbon atoms, before collecting an aliquot of the gaseous stream as a sample in step e1).
- 30 6. The process according to any one of the preceding claims, wherein after the aliquot of the gaseous stream is collected, the gaseous stream is combined with one or more further gaseous stream(s) separated from further conversion effluent(s) obtained by refining further

refinery feed(s) in further conversion unit(s), wherein the further gaseous stream(s) optionally has/have lower biogenic carbon content than the gaseous stream or essentially no biogenic carbon content, and the gaseous stream is subjected to the sweetening treatment in step d) as combined with said further gaseous stream(s).

- 5 7. The process according to any one of the preceding claims, wherein in step b) the conversion effluent comprises at least H₂S, carbon oxide(s) and hydrocarbons; and in step c) the gaseous stream comprises at least H₂S, carbon oxide(s) and C₁-C₃ hydrocarbons.
8. The process according to any one of the preceding claims, wherein the aliquots of the unstabilised naphtha stream are collected intermittently and preferably in step e1) the
10 aliquots of the gaseous stream are collected intermittently.
9. The process according to any one of the preceding claims, wherein in step e2) the selective H₂S removal treatment comprises adsorption, preferably adsorption predominantly based on chemisorption, and/or adsorption on at least one or more metal oxide(s).
- 15 10. The process according to any one of the preceding claims, wherein in step e3) the drying is based on dehydration using at least one or more synthetic polymers, preferably ionomers, more preferably sulfonated tetrafluoroethylene based fluoropolymer-copolymers.
11. The process according to any one of the preceding claims, wherein a portion of the selectively H₂S depleted and optionally dehydrated sample is subjected to a composition
20 analysis using gas chromatography (GC).
12. The process according to any one of the preceding claims, wherein in step f), at least one or more distillate(s) and a fractionation bottom are further separated from the degassed hydrocarbon stream, and the biogenic carbon content in all the recovered distillate(s) and in the fractionation bottom are determined, preferably using accelerator mass spectrometry
25 (AMS) technique.
13. A system for producing hydrocarbons having biogenic carbon content, the system comprising:
- a) at least one or more refinery feed tank(s) configured to receive a refinery feed having biogenic carbon content, non-biogenic carbon content and sulphur content, or components
30 of the refinery feed;

- b) a conversion unit in fluid communication with the refinery feed tank(s), and configured to receive and refine the refinery feed to obtain a conversion effluent comprising at least H₂S and hydrocarbons, and preferably also carbon oxide(s);
- c) a separation section in fluid communication with the conversion unit and configured to receive the conversion effluent and to separate therefrom a gaseous stream and optionally an unstabilised naphtha stream both comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons, and a degassed hydrocarbon stream, wherein the separation section is optionally further configured to separate from the degassed hydrocarbon stream at least one or more distillate(s) and a fractionation bottom;
- d) a sweetening unit in fluid communication with the separation section and configured to receive and sweeten the gaseous stream to obtain a sweetened gas stream; and
- e) a sample treatment and analysis system comprising:
- e1) a sampler in communication, preferably in fluid communication, with the separation section and configured to collect as a sample an aliquot of the gaseous stream at a location upstream of the sweetening unit,
 - e2) a selective H₂S removal unit in communication, preferably in fluid communication, with the sampler and configured to receive the sample and to selectively remove H₂S from the sample to obtain a selectively H₂S depleted sample,
 - e3) an optional drying unit in communication, preferably in fluid communication, with the selective H₂S removal unit and configured to receive and dehydrate the selectively H₂S depleted sample to obtain a dehydrated sample, and an optional gas chromatography (GC) analyzer in communication, preferably in fluid communication, with the selective H₂S removal unit optionally via the drying unit and configured to receive a portion of the selectively H₂S depleted and optionally dehydrated sample, and
 - e4) a biogenic carbon content analyzer, preferably using accelerator mass spectrometry (AMS) technique, in communication, preferably in fluid communication, with the selective H₂S removal unit optionally via the drying unit, and configured to receive at least a portion of the selectively H₂S depleted and optionally dehydrated sample and to determine its biogenic carbon content to obtain the content of biogenic carbon in the gaseous stream.

14. A sample treatment and analysis system comprising:

e1) a sampler configured to collect a sample comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons,

e2) a selective H₂S removal unit in communication, preferably in fluid communication, with the sampler and configured to receive the sample and to selectively remove H₂S from the sample to obtain a selectively H₂S depleted sample,

e3) an optional drying unit in communication, preferably in fluid communication, with the selective H₂S removal unit and configured to receive and dehydrate the selectively H₂S depleted sample to obtain a dehydrated sample, and an optional gas chromatography (GC) analyzer in communication, preferably in fluid communication, with the selective H₂S removal unit optionally via the drying unit and configured to receive a portion of the selectively H₂S depleted and optionally dehydrated sample, and

e4) a biogenic carbon content analyzer, preferably using accelerator mass spectrometry (AMS) technique, in communication, preferably in fluid communication, with the selective H₂S removal unit optionally via the drying unit, and configured to receive at least a portion of the selectively H₂S depleted and optionally dehydrated sample and to determine its biogenic carbon content to obtain the content of biogenic carbon in the collected sample.

15. The sample treatment and analysis system according to claim 14, wherein the collected sample is an aliquot of a gaseous stream comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons; or

wherein the collected sample is an aliquot of an unstabilised naphtha stream comprising H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons, and wherein the sample treatment and analysis system further comprises:

i) a phase separator in communication, preferably in fluid communication, with the sampler and configured to receive the sample and to subject it to phase separation to obtain a gas-phase sample and a liquid naphtha sample, and to pass the gas-phase sample to the selective H₂S removal unit of e2) to obtain in e4) the content of biogenic carbon in the gas-phase sample and to pass the liquid naphtha sample to a biogenic carbon content analyzer to determine its biogenic carbon content to obtain the content of biogenic carbon in the liquid naphtha sample, allowing calculation of the biogenic carbon content in the collected sample based on the contents of biogenic carbon in the gas-phase sample and in the liquid naphtha sample; or

ii) a high-pressure compressor in communication, preferably in fluid communication, with the sampler and configured to receive and compress the collected sample to

obtain a liquefied sample, and to pass the liquefied sample to the selective H₂S removal unit of e2), wherein the system is configured to maintain the liquefied sample in the liquefied state until fed to the biogenic carbon content analyzer of e4).

16. Use of the system for producing hydrocarbons having biogenic carbon content
5 according to claim 13, or of the sample treatment and analysis system of claim 14 or 15, in a process for producing hydrocarbons having biogenic and non-biogenic carbon content, preferably in a process according to any one of claims 1 to 12.

17. Use of the sample treatment and analysis system of claim 14 or 15 for creating and/or
10 training a model for estimating biogenic carbon content of a gaseous stream and/or of an unstabilised naphtha stream in a process for producing hydrocarbons having biogenic carbon content, wherein the gaseous stream and the unstabilised naphtha stream both comprise H₂S and at least one or more of carbon oxide(s) and/or C₁-C₃ hydrocarbons and are obtainable by separating from a conversion effluent obtained by refining in a conversion unit a refinery feed having biogenic carbon content, non-biogenic carbon content and
15 sulphur content; preferably for creating and/or training a model for estimating biogenic carbon content of a gaseous stream and/or of an unstabilised naphtha stream in a process according to any one of claims 1 to 12.