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(54) **Titre : PROCEDE DE PURIFICATION DE COURANTS GAZEUX**
(54) **Title: METHOD OF PURIFYING GAS STREAMS**

(57) **Abrégé/Abstract:**
A method of purifying a gas stream derived from a process wherein a glyceride containing raw-material is converted to hydrocarbon paraffins. The gas stream contains hydrogen or carbon dioxide as a major component and at least one sulphurous component selected from sulphide compounds as an impurity. According to the invention, the gas is contacted with an acidic aqueous wash solution of transition metal ions capable of binding to sulphide ions; a significant portion of the sulphide compounds contained in the gas are bound into practically insoluble transition metal sulphide compounds to remove sulphide compounds from the gas to produce a purified gas; and the obtained purified gas is recovered. The method will efficiently lower sulphide concentrations to ppm or sub-ppm level and it can be implemented on an industrial scale with low investment costs. The metal can be recovered.

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METHOD OF PURIFYING GAS STREAMS

Background of the Invention

Field of Invention

The present invention relates to purification of gas streams. In particular, the present invention concerns a method of purifying a gas stream derived from a process wherein a raw-material containing glycerides, fatty acids or combinations thereof is converted to hydrocarbon paraffins. Such gas streams typically containing a minimum of about 75 vol.-% of hydrogen or carbon dioxide as a major component and at least one sulphurous component selected from sulphide compounds as an impurity.

Description of Related Art

Natural oils and fats are mainly composed of triglycerides. Triglycerides are triesters of fatty acids and glycerol. Vegetable oils and animal fats can contain also some free fatty acids (FFA), which are formed during production of oils and fats through hydrolysis of triglyceride. There raw-materials (in the following also referred to as "glyceride raw-material") can be used as a valuable feedstock for the production of diesel grade fuels.

Conventional approaches for converting vegetable oils or other fatty acid derivatives into liquid fuels comprise transesterification, catalytic hydrotreatment, hydrocracking, catalytic cracking without hydrogen and thermal cracking among others. In the hydrotreatment of vegetable oils (HVO) and animal fats, hydrogen is used to remove oxygen from the triglyceride vegetable oil molecules and to split the triglyceride into separate chains thus creating hydrocarbons. During hydrotreatment, particularly hydrodeoxygenation oxygen containing groups are reacted with hydrogen and removed through formation of water and therefore this reaction requires rather high amounts of hydrogen. Decarboxylation and decarbonylation can occur as side reactions in hydrodeoxygenation producing carbon dioxide and carbon monoxide, respectively.

A catalytic method for the manufacture of hydrocarbons, which are suitable for diesel fuel pool, from renewable sources, such as plant and vegetable oils and fats and animal and fish

oils and fats, is disclosed in EP 1 681 337. The process includes the step of transforming the starting materials into hydrocarbons with minimal consumption of hydrogen, by contacting the starting material with a heterogeneous catalyst comprising at least one metal selected from the metals belonging to the group VIII of the Periodic Table. The hydrocarbons formed via decarboxylation/decarbonylation reactions have one carbon atom less than the original fatty acid or fatty acid portion of its derivate.

The products obtained by the above-mentioned process have a chemical composition which corresponds to that traditional diesel. They can be blended with fossil diesel, traditional biodiesel (FAME), or used as such in diesel engines.

During the conversion of a glyceride raw-material by deoxygenation reactions, off-gases are formed which, depending on the raw-material and the reaction conditions, contain various concentrations of impurities which impair processing of the raw-material and potentially even the product properties of the final products. Typical impurities are sulphide compounds, such as H_2S and COS, ammonia, and halogenides, such as chloride compounds. The latter compounds are primarily formed during processing of the feed; e.g. nitrogen compounds gives ammonia, and chlorides give hydrochloric acid at the conditions conventionally employed in a hydrodeoxygenation reactor. The concentration of ammonia and chlorides are at the ppm level in gas volumes withdrawn from deoxygenation reactions.

As regards the sulphides, there are various sources. In a hydrodeoxygenation reactor, the catalyst metals are conventionally active in sulphided form and the presence of sulphur or sulphurous compounds during the operation of the reactor is usually required for maintaining catalyst activity. For this purpose, some sulphur compounds are actively recycled from a point downstream of the process. Another source of sulphur compounds or sulphides is represented by the feed which usually contains minor amounts of sulphide compounds. However, in practice, there is still a need for the introduction of fresh (external) sulphur compounds for process control.

As a result of the cumulative sulphur sources, the effluent gases of the hydrodeoxygenation reactor will contain sulphide compounds typically in concentrations of 10 to 2000 vol.-ppm.

Hydrodeoxygenation is often carried out using excess hydrogen. Then unreacted hydrogen is recovered and recycled. Hydrogen rich off-gas is typically subjected to amine wash using, for example, monoethanolamine (MEA) or diethanolamine (DEA) to remove carbon dioxide. The amine will also remove sulphide compounds which will contaminate the amine and separation of carbon dioxide from the sulphide compounds from the amine compounds requires special arrangement.

For removing impurities, such as sulphides, from carbon dioxide rich gas at least one, conventionally a plurality of separate treatment steps needs to be employed. Thus, typically various absorption materials are utilized for separating sulphur compounds and carbon dioxide. These separation and wash processes are commercially applied for effective CO_2 removal at low sulphur contents. In addition, various heat treatments or guard beds are used.

WO 98/55209 discloses a method and system for removal of sulphur and sulphur-containing compounds from gas flows using aqueous metal salt solutions at acid conditions. The metal is regenerated by treating the sulphide precipitation at higher temperature with hydrogen to yield pure metal and H_2S. The H_2S can be further treated for instance in a Claus unit to give elementary sulphur. WO 98/55209 is directed to the treatment of gas flows obtained of natural gas, coal gas or biogas, and similar hydrocarbon sources, employing high concentrations of the metal salts.

Summary of the Invention

It is an aim of the present invention to remove at least some of the problems of the art and to provide a novel method of purifying gas streams derived from a process wherein a glyceride containing raw-material is converted to hydrocarbon paraffins.

In the present invention, the gas stream is contacted with an acidic aqueous wash solution of transition metal ions capable of binding to sulphide ions. With the transition metal ions a significant portion of the sulphide compounds contained in the gas are bound into practically insoluble transition metal sulphide compounds to remove sulphide compounds from the gas to produce a purified gas. The thus obtained purified gas can be recovered and used as such or conducted to further treatment.

The absorption liquid can be contacted with the gas which is to be purified for example in a column, such as a tray or packed column, but other contacting devices can also be used. The absorption liquid can be applied by spraying or atomizing, although bubbling is not excluded. When absorbing sulphurous compounds to form metal sulphides also acidic compounds, such as hydrogen chloride will become absorbed. Further, the aqueous, metal ion containing solution can be applied in acidic form. In this form, it will be capable of absorbing such as ammonia (NH_3) and hydrogen chloride (HCl) as well as other alkaline and acidic impurities.

The method will efficiently lower sulphide concentrations to ppm or sub-ppm level and it can be implemented on an industrial scale with low investment costs. The metal, in particular transition metal, such as copper, can be recovered.

More specifically, the method according to the present invention is mainly characterized by what is stated in the characterizing part of claim 1.

Benefits of the Invention

Considerable advantages are obtained by the invention. Thus, in the present novel method separate purification phases are combined. Impurities, such as H_2S, COS, NH_3, HCl, some organic compounds and small particles, are absorbed in water solution.

Precipitation of sulphides is a convenient and more advantageous way of purifying H_2S than traditional amine or methanol wash because it gives an additional driving force for mass transfer of H_2S from the gas to the liquid phase. This is due to the fact that H_2S, HS^- and S^{2-} concentrations in the liquid phase are kept small due to the precipitation of S^{2-} as metal sulphide. Using an acidic wash solution, also ammonia can be washed out from the gas.

The present process can be used in a plant producing hydrocarbon compositions which are suitable as such as diesel fuels or which can be processed into diesel fuels.

In a particularly preferred embodiment, the washing is carried out in a multi-stage process, for example by counter-current washing. In that embodiment, an aqueous effluent can be

withdrawn which is in practice totally free from metal ions derived from the washing liquid and which can be conducted to further treatment in a conventional waste water processing plant.

It has been found that the implementation of the present method, gives considerable advantages when carried out for gas streams derived from a process wherein glyceride containing raw-material is converted to hydrocarbon paraffins. The gaseous effluent of such a process contains as major component hydrogen or carbon dioxide or, typically, a combination of both.

In an embodiment, the gas stream forming a feedstock of the present method is formed by hydrogen gas containing a maximum of 15 vol-%, for example a maximum of 12 vol-%, in particular about 0.1 to 10 vol-% of carbon dioxide.

The gaseous effluent of the above-mentioned process can be treated as such, or either of the two major components can be separated from the other and then treated by the present method.

The carbon dioxide can be separated from recycled hydrogen gas, for example by chemical (e.g. amine) or physical processing and washing (in the following "washing process") and obtained from the regenerator of said washing process. When such a gas stream is treated by a method according to the present invention, the resulting carbon dioxide is very pure; the purified carbon dioxide gas typically meets foodstuff quality parameters and is suitable also for final deposition of the carbon dioxide.

In another embodiment, recycled hydrogen (containing carbon dioxide) of a decarboxylation process is first conducted to a treatment process according to the present invention followed by a carbon dioxide washer. Sulphides, such as hydrogen sulphide, mixtures thereof or other sulphur-containing compounds are thereby first removed. The carbon dioxide of this purified gas stream, in particular hydrogen gas stream, can be subjected to amine wash, physical absorption e.g. in methanol, or another process designed for treatment of carbon dioxide. This subsequent process step for treating carbon dioxide becomes more facile when there are no or practically no sulphide compounds, in particular

no or practically no hydrogen sulphide. Removal of sulphide (such as hydrogen sulphide) simplifies, for example, amine wash considerably.

To mention an example applicable to the above embodiments, when hydrogen sulphide is removed from carbon dioxide gas, at least 95 %, preferably at least 98 %, advantageously at least 99.5 %, of the hydrogen sulphide is removed from the gas, which gives carbon dioxide containing less than 1 vol-ppm of hydrogen sulphide, in particular less than about 500 ppb, in particular less than about 250 ppb by volume.

Brief Description of Drawings

Figure 1 is a graphical depiction of the results of Example 1, showing the proportion of captured H_2S in vol.-ppm as a function of time;
Figure 2 is a graphical depiction of the results of Example 2, showing the proportion of captured H_2S in vol-ppm as a function of time;
Figure 3 is a graphical depiction of the results of Example 3, showing the proportion of captured H_2S in vol-ppm as a function of time; and
Figure 4 is a graphical depiction of the results of Example 4, showing the proportion of captured H_2S in vol-ppm as a function of time.

Description of Embodiments

For the sake of order it should be pointed out that the preferred embodiments are discussed with particular reference to copper sulphate as an absorbing metal salt compound. Although copper sulphate is very efficient and preferred in many embodiments, other salts, in particular transition metal salts, which will be discussed later, can also be used in the same embodiments.

To the extent that numerical values and numerical ranges are indicated it should be noted that the approximate ("about") values are to be interpreted as also including the exact values.

As mentioned above, the present invention relates to purification of gas obtained by conversion of glyceride raw-material into hydrocarbon paraffins, useful as fuels or fuel components.

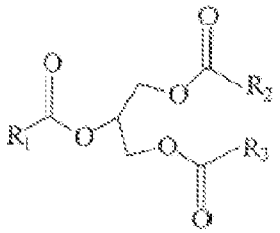
In particular, the present technology provides a method of purifying a gas stream derived from a process wherein a glyceride containing raw-material is converted to hydrocarbon paraffins. Thus, the gas is, in particular, derived from a process in which the glyceride raw-material is contacted with hydrogen, such reaction being exemplified by catalytic hydrotreatment of triglycerides comprising hydrogenation of double bonds in fatty acid chains and hydrodeoxygenation of triglyceride (decomposition of triglyceride structure).

However, the present method can also, equally well, be used for gas streams which are derived from conversion processes, such as decarboxylation, in which only minor concentrations of hydrogen, if any, are employed.

A great variety of raw-materials can be processed by the above processes. Thus, suitable glyceride containing raw-materials for use in the process are typically selected from the group of biological oils, natural fats and various combinations thereof.

Thus, in the present context, the "glyceride containing raw-material" denotes for example a feedstock which comprises for instance various oils and/or fats originating from biological and renewable sources, e.g., fats and oils originating from plants and/or animals and/or fish and compounds derived from them as well as oils and fats and oils obtained from microbiological processes. Said oils and fats typically comprise $C_{10} - C_{24}$ fatty acids, derivatives thereof, such as esters of fatty acids as well as triglycerides of fatty acids or combinations of thereof. Fatty acids or fatty acid derivatives, such as esters may be produced via hydrolysis of said oils and fats or by their fractionalization or transesterification reactions of triglycerides or by microbiological processes utilizing algae or microbes, such as yeasts, molds or bacteria.

The basic structural unit of said oil or fat is a triglyceride, but typically also diglycerides and free fatty acids are comprised therein. Triglyceride is a triester of glycerol with three fatty acid molecules, having the structure presented in the following formula I:



Formula I. Structure of triglyceride

In Formula I, R_1, R_2 and R_3 are alkyl chains. Fatty acids found in natural triglycerides are almost solely fatty acids of even carbon number. Therefore R_1, R_2, and R_3 typically are C_5 – C_{23} alkyl groups, mainly C_{11}-C_{19} alkyl groups and most typically C_{15} or C_{17} alkyl groups. R_1, R_2, and R_3 may contain carbon-carbon double bonds. These alkyl chains can be saturated, unsaturated or polyunsaturated. In case one of the R_1, R_2 or R_3 is hydrogen, then Formula I represents diglycerides, and if two of these are hydrogen then the formula represents a monoglyceride, which both might be present in oils and fats, especially in their processing products.

The natural fat as a "glyceride containing raw-material" is typically an animal or plant fat or oil (here, oils are defined as fats) selected from: the lauric-myristic acid group (C_{12} to C_{14}) including milk fats, as well as coconut oil, palmseed oil, babassu oil, muscat butter oil, laurel seed oil; from the palmitic acid group (C_{16}) including earth animal fats, as well as palm oil and stillingia tallow; the stearic acid group (C_{18}) including fats of earth animals, as well as cocoa butter, shea butter and Borneo tallow; the oleic and linoleic acid group (unsaturated C_{18}) including whale and fish oils as well as tall oil (fatty acid fraction), rapeseed or canola oil, olive oil, peanut oil, sesame oil, maize oil, sunflower oil, poppy seed oil, cottonseed oil and soy oil; the linolenic acid group (unsaturated C_{18}) further including linseed oil, perilla oil and hemp oil; the erucic acid group (unsaturated C_{22}) including whale and fish oils as well as rapeseed oil and mustard seed oil; the eleostearic acid group (conjug. unsaturated C_{18}) including whale and fish oils as well as Chinese wood oil; and fats with substituated fatty acids (ricinoleic acid, C_{18}) such as castor oil. Suitable oils or fats are also Jatropha seed oils as well as fats and oils originating from processes using microbes, such as algae, bacteria, yeasts and moulds.

Derivatives of natural fats include mono- or diglycerides of C_{10} to C_{28} fatty acids, C_{10} to C_{28} fatty acids, C_{10} to C_{28} fatty acid anhydrides, non-glyceride C_{10} to C_{28} fatty acid esters, C_{10} to C_{28} fatty alcohols, C_{10} to C_{28} fatty aldehydes and C_{10} to C_{28} fatty ketones. The C_{10} to

C_{28} fatty acids, their mono- and diglycerides, as well as their anhydrides are typically prepared by hydrolysis of the corresponding triglyceride. The non-glyceride C_{10} to C_{28} fatty acid esters are mainly prepared from the triglycerides by transesterification. The C_{10} to C_{28} fatty alcohols, aldehydes and ketones are prepared by reduction, usually by hydrogenation, of the corresponding fatty acids.

The derivatives of natural fats also include any of the aforementioned natural fats and derivatives, the hydrocarbon chain of which has been modified e.g. by substitution, branching or saturation.

The natural fats or derivatives thereof can be provided in pure form or as part of a feedstock containing other components. The triglycerides can also be prehydrogenated in order to reduce unsaturation, sulphur and nitrogen content.

Fuels or fuel components can be obtained from the raw-materials by a number of processes. Examples include:

- hydrogenation of fatty acids, their esters and glycerides, including mono-, di- and triglycerides;
- hydrodeoxygenation of fatty acids, their esters and glycerides, including mono-, di- and triglycerides; and
- hydrocracking of fatty acids, their esters and glycerides, including mono-, di- and triglycerides.

Further, the present method can be applied to remove sulphide compounds from a gas rich in carbon oxides produced by a decarb reaction selected from decarboxylation and decarbonylation reactions and combinations thereof, wherein one-less-carbon n-paraffins are produced from the analogous fatty acids or carboxylic acid parts of glycerides along with carbon oxides.

It is also possible to combine said processes.

Herein, by “deoxygenation” is meant partial or complete removal of oxygen from the molecules of the above-mentioned glycerides, i.e. triglycerides, fatty acids, fatty acid

analogues or derivatives. The deoxygenation operation may involve, for example, hydrogenation (reaction with hydrogen).

The process also comprises steps involving hydrolysis (reaction with water), decarbonylation (removal of carbonyl as carbon monoxide) and/or decarboxylation (removal of carboxyl as carbon dioxide).

Products of a deoxygenation step comprise aliphatic C_9 to C_{28} hydrocarbons, preferably aliphatic C_{11} to C_{24} hydrocarbons, more preferably aliphatic C_{11} to C_{20} hydrocarbons, in particular aliphatic C_{15} to C_{18} hydrocarbons.

C_9 to C_{28} hydrocarbons obtained from deoxygenation typically exhibit low amounts of unsaturation and heteroatom impurities. Such hydrocarbons are especially suitable for hydroisomerization to produce diesel fuel/components or for hydrocracking to form lower hydrocarbons. Optionally the hydrocracking is carried out after a purification step.

In hydrocracking aliphatic light hydrocarbons are formed such as gasoline. Thus, it is preferred to produce by the hydrocracking step aliphatic C_2 to C_{14} hydrocarbons, such as aliphatic C_2 to C_8 hydrocarbons, i.e. light gasoline.

A particularly advantageous process for deoxygenating starting materials originating from renewable sources is the one mentioned above (EP 1 681 337) which comprises an alternative reaction route – decarboxylation/decarbonylation, where oxygen is removed in the form of CO and CO_2 from the original compounds in the starting material/feedstock. In this way hydrocarbons can be manufactured from plant and vegetable oils and fats as well as animal and fish oils and fats without high consumption of hydrogen. In the process for manufacturing hydrocarbons in the diesel fuel distillation range from renewable sources, hydrogen is required only for the reduction of the catalyst. The content of EP 1 681 337 is herewith incorporated by reference.

The present method will be applied to a gas stream obtained from any of the above processes.

The gas stream contains gaseous (non-condensable) components, such as hydrogen or carbon dioxide or combinations thereof, which make up a large majority of its volume. Typically at least 75 vol.-%, in particular at least 80 vol.-% and up to about 99 vol.-%, of the gas stream is formed by hydrogen or carbon dioxide.

Thus, for example a hydrogen gas flow subjected to a treatment according to the present invention contains always some other gas components and some impurities, in particular impurities in the form of other gaseous components. Although the concentration of such impurities is relatively small, it may still be significant enough to impair further treatment of the main gas components of the gas stream. As explained above, particularly interesting sources of gas streams intended for the present treatment are processes in which fatty acids, their esters and glycerides, including mono-, di- and triglycerides are hydrogened, hydrodeoxygenated and/or hydrocracked, in general decarboxylated.

Decarboxylation generates carbon dioxide which should be recovered as pure as possible with regard to further use. In order to achieve this aim, sulphides, in particular hydrogen sulphide, and similar sulphur-containing compounds should be separated. The recovery process can be directed towards the gas composition circulating in the recycle line of the hydrogen gas, for example in a decarboxylation process.

It should be noted that the step of contacting the gas with the wash solution (which will be described below) can, if so needed, be preceded by at least one purification step of the gas, wherein the carbon oxide – in particular carbon dioxide rich – gas to be treated is an off-gas of the process.

Thus, to take an example, the present washing method can be carried out on a carbon dioxide -rich gas recovered from amine washing.

In addition to one or several main components there are also minor components. Such low-concentration compounds may include lower hydrocarbons. Importantly there are, however, sulphurous components. These impurity components are typically formed by sulphide compounds, such hydrogen sulphide (H_2S), carbonyl sulphide (COS) or organic sulphides or combinations and mixtures of such compounds. In practice the gas may contain at least 0.1 vol.-ppm of sulphide compounds, in particular about 1 vol.-ppm to 1 vol.-%, preferably about 3 to 5000 vol.-ppm, of sulphide compounds.

A hydrogen-rich gas contains in addition to sulphides also typically and other gaseous impurity components, such as carbon monoxide, carbon dioxide or lower alkanes, such as methane, ethane, propane and butane(s), or combinations thereof.

According to one embodiment, which relates to the treatment of a hydrogen-rich gas, the gas to be purified is a recycle gas discharged from an HDO reactor. The gas is cooled whereby the heaviest hydrocarbons and water are mainly condensed.

In another embodiment, the carbon dioxide containing gas is generated in the regeneration step of an amine solution emanating from a conventional amine purification system wherein dissolved gases in the amine are released before the amine solution is recycled.

The temperature of the gas is generally about 20 to 70 °C, typically 30 to 50 °C, advantageously about 40 °C.

The gas is contacted with an acidic aqueous wash solution of transition metal ions capable of binding to sulphide ions, and a significant portion of the sulphide compounds contained in the gas are bound into solid sulphides which have low solubility and which can therefore be precipitated from the solution.

In a preferred embodiment, the present invention carried out by contacting the gas with an acidic aqueous wash solution containing transition metal ions capable of binding to sulphide ions of the sulphide compounds present in the gas. The concentration of the transition metal cations can be small, for example the aqueous solution has a concentration in respect of the transition metal ion(s) is 0.00001 M to 0.1 M, for example 0.00001 M to 0.01 M, typically about 0.00005 M to 0.005 M preferably about 0.0001 M to 0.001 M .

In a preferred embodiment, the metal ions, i.e. cations, of the wash solution are derived from transition metals selected from the group of copper, zinc, iron and cobalt and mixtures thereof, in particular from copper, zinc and iron and mixtures thereof. Advantageously, the metal ions of the wash solution comprise bivalent metal cations of copper, zinc and iron and mixtures thereof.

The transition metal ions are obtained from water soluble metal salts by dissolving said salts in water. In one embodiment, the aqueous solution is prepared by dissolving about 1 to about 10,000 parts, preferably about 50 to about 5,000 parts by weight of a metal salt into 1,000,000 parts by weight of water.

For the preparation of suitable wash solutions the water soluble metal salts of the above mentioned cations can comprise an anion selected from the group of anions derived from inorganic acids, such as sulphate, sulphite, phosphate, phosphite, nitrate, chloride and carbonate and mixtures thereof. Anions derived from simple organic acids (typically of the kind having no more than 10 carbon atoms for example 6 or less carbon atoms) are also possible. Examples of such anions are citrate, malonate and acetate and mixtures thereof.

Based on the above, specific non-limiting examples of anions include the following: sulphate, sulphite, bisulphite, thiosulphate, chloride, iodide, phosphate, monobasic phosphate, dibasic phosphate, hypophosphite, dihydrogen pyrophosphate, carbonate, bicarbonate, metasilicate, citrate, malate, maleate, malonate, succinate, lactate, formate, acetate, butyrate, propionate, benzoate, tartrate, ascorbate and gluconate.

With reference to the above, in a particularly preferred embodiment, the combinations of the metal cations and anions are selected such that the metal salt obtained is water soluble.

The salt may also be a hydrated salt. Such salts are typically crystalline salt hydrates with one or more bonded water molecules of crystallization.

$CuSO_4$ solution can be prepared either by dissolving $CuSO_4$ powder in water or reacting CuO powder with a solution of H_2SO_4 and water. In the first case, H_2SO_4 formed has to be removed from any circulating washing fluid. In the second case H_2SO_4 formed will react with CuO producing the desired Cu^{2+} and SO_4^{2-} ions. Additionally metallic Cu powder with H_2SO_4 water solution produces $CuSO_4$ water solution and hydrogen.

In a preferred embodiment, the aqueous wash solution is acidic or weakly acidic; preferably it has a pH of about 1 to about 6.5, in particular about 1 to about 5. The pH will vary within the indicated range depending on the metal cations.

The molar ratio of the metal ion to sulphide compounds of the gas to be purified is in excess of about 1, preferably about 1.4 to about 6, in particular about 1.5 to about 5.5, advantageously about 2 to about 4.5.

To take an example, aqueous copper sulfate precipitates hydrogen sulfide as copper sulfide according to Formula I:

$$Cu^{2+} + H_2S + SO_4^{2-} \rightarrow CuS + 2\ H^+ + SO_4^{2-} \quad (1)$$

Generally, the absorption of H_2S from the gas to be treated into Me-SO_4-water solution (wherein Me stands for a metal, in particular a transition metal, such as copper, iron, zinc or cobalt) is a mass transfer limited process. H_2S has to be dissolved in liquid phase where the reaction of H_2S and Me-SO_4 takes place fast. Me^{2+} ions and H_2S have to be present in liquid film where the reaction takes place and mass transfer of H_2S and Me^{2+} ions into liquid film are limiting the reactions. Reaction of Me^{2+} ions with H_2S forms MeS, which will precipitate as small crystals effectively because of small solubility of the sulphide in water.

The crystals are formed by nucleation and crystal growth mechanisms. The nucleation and crystal growth rate depend on the supersaturation of Me^{2+} and S^{2-} ions in film. Mass transfer may depend also on nucleation rate, which affects the Me^{2+} and S^{2-}concentrations.

Thus, a significant portion of the sulphide impurities present and contained in the gas can be converted into the form of transition metal sulphide compounds. The sulphide compounds so formed are preferably precipitated into the wash solution whereby the sulphide impurities are removed from the gas. The purified gas so obtained is separated from the aqueous solution.

Preferably a significant portion of the hydrogen sulphide impurities contained in the gas are bound into practically insoluble (i.e. sparingly soluble) transition metal sulphide compounds.

Also other components in the gas to be treated, such as CO_2, NH_3, can be dissolved and reacted.

The pH of the ion system has to be within a specific range depending on the metal ion used. To take an example, for copper, i.e. Cu^{2+}, pH should be approximately within the range of 1 to 5.2 to prevent precipitation of other components than CuS, such as $CuCO_3$, $Cu(OH)_2$, and $(NH_4)_2SO_4$ depending on the $CuSO_4$-water solution concentration and gas composition, and the total pressure and temperature.

Additionally H_2S is precipitated from liquid as sulphides with metal ions. Because the solubility of metal sulphides is very small, lean metal ion concentrations can be used and efficient precipitation is still achieved.

By the method, a significant portion of the hydrogen sulphide is removed from the gas. In particular at least 95 %, preferably at least 98 %, advantageously at least 99.5 %, of the hydrogen sulphide is removed from the gas. The concentration of hydrogen sulphide of the purified gas is, generally, less than about 500 ppb, in particular less than about 250 ppb by volume. In one embodiment, the concentration of hydrogen sulphide of the purified gas is less than about 100 ppb.

Generally, the gas is contacted with the wash solution at a temperature in the range of 10 and 80 °C and at a pressure in the range from 1 to 50 bar (absolute pressure). Thus, the washing can be carried out at ambient temperature and pressure (20 to 25 °C and 1 bar(a)), although it is equally possible to work the present technology at lower temperatures (10 to <20 °C) and at elevated temperatures (>25 to 80 °C). The pressure can be in excess of 1 bar(a), for example about 1.5 to about 50 bar(a).

There are several options for contacting of the gas with the washing liquid/absorption medium.

In a first preferred embodiment, the contacting of the gas with the absorption medium takes place by spraying or atomizing the absorption medium into the gas. Preferably, the contacting of the gas with the absorption medium takes place in the interface between the gas and droplets of the absorption medium.

In this embodiment, the step of contacting the gas to be purified with the wash solution comprises spraying droplets of the wash solution into the gas, maintained in gaseous phase, and precipitating the absorbed sulphur compound in the form of solid metal sulphide in the droplets of the wash solution.

The wash solution can be contacted with the gas in a spray chamber having an essentially vertical central axis, said gas being fed into the spray chamber so as to advance in the direction of the central axis of the spray chamber and the wash solution being fed through spray nozzles arranged in as one or more spray zones in series along the central axis at different heights in the spray chamber.

Furthermore, in a practical embodiment the gas is fed into the spray chamber via gas distributors arranged below the lowest spray zone, and the metal sulphide is withdrawn from the reactor along with the used wash liquid via an outlet arranged in the bottom part of the chamber.

In a second preferred embodiment, the gas to be purified is bubbled into a stirred tank containing the absorption solution.

In a third embodiment, absorption towers with plates and/or packing can be used in a counter-current operation. The detailed equipment type depends on the concentration of the metal ions in the solution and the amount and impurity content of the gas.

Generally, the wash solution contains less than 1500 wt-ppm as metal, preferably less than 1000 wt-ppm, in particular about 10 to about 450 wt-ppm, of a copper salt, advantageously copper sulphate.

In some embodiments, washing is performed in several steps, in which the concentration of the washing liquid can be the same or different. One particular embodiment, washing liquids having 2 or more different concentrations are employed. Thus, in a first stage, the inlet gas is contacted with a washing liquid which contains less than a stoichiometric amount of metal ions with respect to the sulphide compounds present, and in a second stage of the process, the gas treated is contacted with a washing liquid which contains an excess of metal ions with respect to the sulphide compounds present in the gas.

Washing is, in the embodiment, preferably carried out such that the gas to be purified will first meet a solution that has a first concentration of Cu^{2+} ions, whereas at the last contact point between the gas and the washing solution the washing solution will have a second concentration of Cu^{2+} ions, said second concentration being at least 2 times, preferably at least 5 times greater, in particular 10 times greater, than the first concentration.

The recovered purified gas can be fed to further processing, e.g. to amine washing.

A purified hydrogen-rich gas can be used, potentially combined with fresh feed, for hydrotreatment of triglyceride raw-material, in particular in a process for hydrotreating in a hydrotreating step and the isomerising in an isomerisation step a feed of biological oils, natural fats and their processing products, such as free fatty acids and stearin or combinations thereof.

Based on the above, in one embodiment, the present invention comprises a method of processing a glyceride containing raw-material and of treating a gas stream, comprising the steps of

- converting a glyceride containing raw-material to hydrogen paraffins;
- optionally recovering said hydrogen paraffins;
- recovering from the converting step a gas stream containing a minimum of about 75 vol-% of hydrogen or carbon dioxide as a major component and at least one sulphide compound as an impurity;
- contacting the gas with an acidic aqueous wash solution of transition metal ions;
- binding a significant portion of the sulphide compounds contained in the gas into practically insoluble transition metal sulphide compounds; and
- separating the formed metal sulphide compounds together with the wash solution from the gas to obtain the purified gas.

This method can be combined with any of the embodiments discussed above. Thus, the various method steps can be carried out as explained above.

The following examples are given for illustrative purposes only.

Experimental

Equipment

In the following experiments a laboratory equipment set up was employed in which gas to be purified was passed from a pressure vessel through a pressure regulator and a mass flow meter and then bubbled into a glass bottle near the bottom. The solution in the bottle was agitated with a magnetic stirrer to improve mass transfer between gas and liquid phase. When the gas bubbles rose up from the solution a slight over-pressure was generated in the bottle which forced the gas to enter the outlet tube. The tube was provided with a nozzle to which a H_2S selective Dräger-tube was connected. After the Dräger-tube the gas entered a Ritter drum-type gas meter and from there it was conducted to ventilation. It was possible to by-pass the Dräger-tube by suitably turning valves in the tubing.

The mass flow meter was calibrated for CO_2 in Examples 1 and 2, where 100 vol-ppm H_2S in CO_2 gas was used. In Examples 3 and 4 the same mass flow meter was used without new calibration, so that the mass flow meter was only used for flow value setting and the results are calculated based on the Ritter drum-type gas meter that was installed as the last equipment before the gas entered the ventilation.

In Examples 3 and 4, the gas was coming from a special gas sample bomb of 1 gallon volume, ordered just for these tests. The gas used was taken from a hydrogen stream of an industrial process treating natural fats by hydrodeoxygenation.

Only the H_2S content of the gas coming out from the absorber bottle was analyzed because the other gases did not dissolve in the $CuSO_4$ solution. Normally, Dräger-tubes are used so that a certain volume of gas is pumped through the tube and the colour change in the tube indicates the H_2S content of the gas. In the present experiments the gas passed through the Dräger-tube for a certain time and the indication of the Ritter drum-type gas meter was recorded.

The solution pH was measured before and after the experiment. The precipitated CuS solid was not analysed in these tests.

All experiments were carried out at laboratory temperature; heating or cooling was not used. The temperature was approximately between 20 and 25 °C.

Materials

A $CuSO_4$ solution was prepared using $CuSO_4 \cdot 5H_2O$ and ion exchanged water. First, a solution of 15 mass-% was prepared and all solutions used were then diluted from it. The concentrations employed were 0.005 mass-% $CuSO_4$, 0.01 mass-% $CuSO_4$, 0.05 mass-% $CuSO_4$, and 0.1 mass-% $CuSO_4$.

The gas in Examples 1 and 2 was supplied by AGA. It contained 100 vol-ppm of H_2S in CO_2. This delivered pressure vessel had initially a higher pressure, but it was reduced to 10 bar (abs.) using a pressure regulator. This gas was then passed through a mass flowmeter, which was calibrated for CO_2.

In Examples 3 and 4 gas from a hydrogen stream of a natural fat hydrodeoxygenation process was obtained using a 1 gallon gas sample bomb. The analysis of this gas was obtained from the process on-line analyser of the gas stream.

Example 1

The test was carried out using the following materials:

Gas: AGA, 100 vol-ppm H_2S in CO_2
Gas bottle outlet pressure regulated to 10 bar (abs.)
Gas flow adjusted with mass flow meter: 10 litres/hour
$CuSO_4$ solution: 0.01 mass-% $CuSO_4$ in ion exchanged water, pH 5, 250 ml
Dräger-tubes: range 5–60 vol.-ppm H_2S (1 litre of gas used in analysis)

The pH of the prepared $CuSO_4$ solution was measured using a pH indicator paper. Then, 250 ml of this 0.01 mass-% $CuSO_4$ solution was placed in the absorption bottle. The magnetic stirrer bar was added to bottle and the bottle was closed. All gas lines were checked and correct valves opened.

The mass flow meter was set to 10 litres/hour. The pressure regulator of the gas bottle was set to 10 bar (abs.). Then the gas flow was started. The Ritter drum-type gas meter indication and time was recorded.

Then Dräger-tubes for the range 5–60 vol.-ppm H_2S were used. As the gas flow through the Dräger-tube was started the time and Ritter drum-type gas meter indication were recorded. When a suitable volume of the gas had passed through the Dräger-tube the gas flow was directed through the bypass by opening and closing valves. Again at that point the time and Ritter drum-type gas meter indication were recorded in addition to the reading from the Dräger-tube. Then the Dräger-tube was changed to a new one and the H_2S content measurement was repeated. The experiment continued to the point that the Dräger-tube measurement indicated that the H_2S content is the same as in the feed of the absorption bottle. This also means that all copper(II) ions have been depleted from the solution.

The H_2S vol.-ppm values were measured from the outlet gas of the $CuSO_4$ absorption bottle.

The pH of the solution was 5 after the test.

Table 1. Results of copper sulphate washing of laboratory gas

Time	Ritter, litres	Dräger in use	Gas flow through Dräger-tube, litre	Dräger-tube indication, vol-ppm	H_2S-content in gas, vol-ppm	Notes
9:13	Gas flow on					
9:20	355033.45					
9:22	355033.80	Start				
9:27	355034.40	Stop	0.60	3	5	Small particles
9:39	355036.45	Start				
9:41	355036.65	Stop	0.20	1	5	More particles
10:02	355040.20	Start				
10:06	355040.70	Stop	0.50	3	6	
10:26	355044.20	Start				
10:30	355044.70	Stop	0.50	3	6	
11:36	355055.80	Start				
11:40	355056.40	Stop	0.60	10	16.7	
12:32	355065.20	Start				
12:36	355065.80	Stop	0.60	12	20	
13:11	355071.70	Start				
13:14	355072.20	Stop	0.50	20	40	
14:26	355084.30	Start				
14:29	355084.82	Stop	0.52	50	96	
14:53	355088.80	Start				
14:56	355089.30	Stop	0.50	50	100	
14:57	Gas flow off					

The results are also shown graphically in Figure 1.

From the balances it can be calculated that 250 ml of 0.01 mass-% $CuSO_4$ solution contains $156.6 \cdot 10^{-6}$ moles of Cu. This is the maximum amount of moles of H_2S that can be removed from the gas as solid CuS. The balance calculation gives that the processed gas contained a total of $249.0 \cdot 10^{-6}$ moles of H_2S. The balance calculation shows that in this case 67.2 % is the maximum amount of H_2S that could have been removed.

The actual result is visible in Figure 1 as the area of captured H_2S. Integration of the captured and non-captured areas using trapezoidal approximation between points gives result that 68.7 % of H_2S have been captured. This result is reasonably accurate taken into account that the analyses were carried out using Dräger-tubes. This means that practically all copper ions from the solution have been depleted and precipitated as CuS.

Example 2

The test was carried out using the following materials:

Gas: AGA, 100 vol-ppm H_2S in CO_2
Gas bottle outlet pressure regulated to 10 bar (abs.)
Gas flow adjusted with mass flow meter: 10 litres/hour
$CuSO_4$ solution: 0.1 mass-% $CuSO_4$ in ion exchanged water, pH 5, 250 ml
Dräger-tubes: range 5–60 vol.-ppm H_2S (1 litre of gas used in analysis)

The bubbling was continued overnight. The measured pH at the end of the experiment was 2, showing that the formation of sulphuric acid have taken place in the solution, i.e. copper ions of the copper(II)sulphate solution have been replaced by H_3O^+ ions formed from water and the hydrogen from the hydrogen sulphide. The copper(II) ions have been combined with S^{2-} ions to form practically insoluble CuS that have been precipitated out of the solution.

The H_2S vol-ppm values were determined at $CuSO_4$ absorption bottle outlet gas.

Table 2. Results of copper sulphate washing of laboratory gas

Time	Ritter, litres	Dräger in use	Gas flow through Dräger-tube, litre	Dräger-tube indication, vol-ppm	H_2S-content in gas, vol-ppm	Notes
7:45	Gas flow on					
7:53	355096.85					
7:56	355097.20	Start				
8:00	355097.70	Stop	0.50	0	0	Small black particles
8:28	355102.40	Start				
8:32	355102.90	Stop	0.50	1	2	
9:32	355113.20	Start				
9:36	355113.70	Stop	0.50	1	2	More particles
10:27	355122.40	Start				
10:31	355139.90	Stop	0.50	1	2	
12:05	355138.90	Start				
12:09	355139.40	Stop	0.50	1	2	
15:21	355171.70	Start				
15:24	355172.20	Stop	0.50	3	6	
1.3.2012-2.3.2012	Bubbling continues overnight					
8:22	355344.30	Start				
8:25	355344.80	Stop	0.50	6	12	A lot of black precipitate
11:57	355380.90	Start				
12:01	355381.40	Stop	0.50	8	16	
13:17	355394.40	Start				
13:20	355394.90	Stop	0.50	11	22	
14:55	355411.00	Start				
14:58	355411.50	Stop	0.50	11	22	
14:59	Gas flow off					

The results are also shown graphically in Figure 2.

From the balances it can be calculated that 250 ml of 0.10 mass-% $CuSO_4$ solution contains $1.566 \cdot 10^{-3}$ moles of Cu. This is the maximum amount of moles of H_2S that can be removed from the gas as solid CuS. The gas flow balance calculation gives that the

processed gas contained a total of $1.404 \cdot 10^{-3}$ moles of H_2S. This means that not all copper ions from the solution have been depleted and precipitated as CuS. The balance calculation shows that in this case 1.116 was the Cu^{2+} ion molar ratio to the H_2S in the totally processed feed. Thus it could have been possible to continue the test and remove more hydrogen sulphide from the gas.

The actually captured H_2S will appear from Figure 2 as the area over the curve. Integration of the captured and non-captured areas using trapezoidal approximation between points gives result that 90.7 % of H_2S fed through the $CuSO_4$ solution have been captured.

Again this experiment was carried out as one mixed stage. If the gas bubbles have been smaller, e.g. using a sinter in the gas feed to the bottle, the mass transfer would have been better and the percentage of the captured H_2S would have been higher. Due to the possible blockage of the sinter pores with solid CuS the sinter was not used. Also, it can be concluded that by proper design of a continuous multistage counter current absorber the cleaned gas would contain H_2S on the ppm or sub-ppm level.

Example 3

The equipment used was the same as in Examples 1 and 2. In the present example and in Example 4 below the feed gas was provided by a special one gallon (3.8 litres) sample bomb filled into 20 bars in the process and connected to the feed gas line in the laboratory.

The test was carried out using the following materials:

Gas: Gas from a hydrogen stream of a natural fat hydrodeoxygenation process analysis given in Table 3. The particular gas sample was taken into special 1 gallon sample bomb.

Table 3. Analysis of the gas from a hydrogen stream of a natural fat hydrodeoxygenation process

Component	Concentration, mol-%
Hydrogen	93.3
Carbon monoxide	0.41
Carbon dioxide	1.73
Hydrogensulphide	<0.1
Methane	1
Ethane	0.2
Propane	3.2
C2+C3	3.4
C4 Total	0.1
	Concentration, ppm
Ammonia	<2

Gas sample bomb outlet pressure regulated to 5 bar (abs.)
Gas flow adjusted with mass flow meter: 10 litres/hour
$CuSO_4$ solution: 0.005 mass-% $CuSO_4$ in ion exchanged water, pH 5, 250 ml
Dräger-tubes: range 5–60 vol.-ppm H_2S (1 litre of gas used in analysis)

The feed gas sample bomb was kept in a thermo stated (+20 °C) shelter outside to guarantee even quality of the feed gas (no condensation of heavy components) during the experiments.

The solution pH after the test was 5. The pH value did not change in this test. The H_2S vol-ppm values were determined at $CuSO_4$ absorption bottle outlet gas.

The results of the copper sulphate washing are given in Table 4:

Table 4. Results of copper sulphate washing of industrial gas

Time	Ritter, litres	Dräger in use	Gas flow through Dräger-tube, litre	Dräger-tube indication, vol-ppm	H_2S-content in gas, vol-ppm	Notes
9:37	Gas flow on					
9:40	355415.66					
9:44	355416.55	Start				
9:47	355417.05	Stop	0.50	28	56	Solution light brown
9:57	355419.10	Start				
9:58	355419.40	Stop	0.30	46	153	Solution light brown, no precipitate
10:07	355421.40	Start				
10:08	355421.60	Stop	0.20	51	255	
10:19	355423.90	Start				
10:20	355423.95	Stop	0.05	200	400	A Dräger-tube 10–200 ppm H_2S in 0.1 litres of gas was used
10:32	355426.45	Start				
10:33	355426.60	Stop	0.15	61	407	
10:44	355429.10	Start				
10:45	355429.20	Stop	0.10	45	450	
10:48	355430.00	Gas flow off				

Figure 3 shows the same results in graphical form.

From the balances it can be calculated that 250 ml of 0.005 mass-% $CuSO_4$ solution contains $78.3 \cdot 10^{-6}$ moles of Cu. This is the maximum amount of moles of H_2S that can be removed from the gas as solid CuS. The balance calculation gives that the processed gas contained a total of $127.3 \cdot 10^{-6}$ moles of H_2S. This means that all copper ions from the solution could have been depleted and precipitated as CuS, but that was not the case. The test was too short to use all Cu^{2+} ions from the solution, due to possible mass transfer limitations.

The balance calculation shows that in this case 0.615 was the Cu^{2+} ion molar ratio to the H_2S in the totally processed feed.

The actually captured H_2S is visible in Figure 3 as the area over the curve. Integration of the captured and non-captured areas using trapezoidal approximation between points gives result that 33.0 % of H_2S fed through the $CuSO_4$ solution have been captured.

Example 4

The same equipment that was used previously in Example 3 was also used in this test. As pointed out, in Examples 3 and 4, the feed gas was provided by a special one gallon (3.8 litres) sample bomb filled into 20 bars in the process and connected to the feed gas line in the laboratory. The sample bomb was filled again in process after the test of Example 3.

The test was carried out using the following materials:

Gas: Gas from a hydrogen stream of a natural fat hydrodeoxygenation process analysis given in Table 3. The gas was taken into special 1 gallon sample bomb.
Gas sample bomb outlet pressure regulated to 5 bar (abs.)
Gas flow adjusted with mass flow meter: 10 litres/hour
$CuSO_4$ solution: 0.05 mass-% $CuSO_4$ in ion exchanged water, pH 5, 250 ml
Dräger-tubes: range 5–60 vol.-ppm H_2S (1 litre of gas used in analysis)

The results of the copper sulphate washing are given in Table 5. H_2S vol-ppm values were determined from the outlet gas of the $CuSO_4$ absorption bottle.

The solution pH after the test was 3. This indicates that sulphuric acid has been formed into the solution.

During the test the feed bomb run out of gas and thus the end of this test is not reliable.

Table 5. Results of copper sulphate washing with industrial gas stream

Time	Ritter, litres	Dräger in use	Gas flow through Dräger-tube, litre	Dräger-tube indication, vol-ppm	H_2S-content in gas, vol-ppm	Notes
9:57	Gas flow on					
10:00	355483.60					
10:03	355484.10	Start				
10:06	355484.60	Stop	0.50	1	2	Solution a little brownish
10:12	355486.10	Start				
10:15	355486.60	Stop	0.50	5	10	Visible precipitate
10:23	355488.40	Start				
10:26	355488.90	Stop	0.50	6	12	More precipitate
10:36	355491.10	Start				
10:39	355491.60	Stop	0.50	11	22	A lot of precipitate
10:52	355494.60	Start				
10:55	355495.10	Stop	0.50	13	26	
11:22	355500.80	Start				
11:25	355495.30	Stop	0.50	19	38	
12:08	355510.50	Start				
12:11	355511.00	Stop	0.50	30	60	
12:48	355518.90	Start				
12:51	355519.40	Stop	0.50	40	80	
13:07	355522.90	Start				
13:09	355523.40	Stop	0.50	48	96	
14:06	355535.50	Start				
14:08	355535.70	Stop	0.20	60	300	
15:08	355548.40	Start				
15:09	355548.55	Stop	0.15	55	367	
15:32	355553.60	Start				
15:33	355553.75	Stop	0.15	62	413	
15:55	355558.65	Start				
15:56	355558.80	Stop	0.15	61	407	
16:07	355560.95	Start				
16:09	355561.05	Stop	0.10	38	380	Feed bomb practically empty
16:10	355561.09	Gas flow off				Feed bomb empty

The same results are shown graphically in Figure 4.

As the feed bomb got almost empty the results are treated only to time 15:33. The rest of data is rejected.

From the balances it can be calculated that 250 ml of 0.050 mass-% $CuSO_4$ solution contains $0.783 \cdot 10^{-3}$ moles of Cu. This is the maximum amount of moles of H_2S that can be removed from the gas as solid CuS. The gas flow balance calculation gives that the processed gas contained a total of $0.624 \cdot 10^{-3}$ moles of H_2S. The balance calculation shows that in this case 1.26 was the Cu^{2+} ion molar ratio to the H_2S in the totally processed feed.

The actually captured H_2S is visible in Figure 4 as the area over the curve. Integration of the captured and non-captured areas using trapezoidal approximation between points gives result that 76.4 % of H_2S fed through the $CuSO_4$ solution have been captured.

Conclusions

The first two examples used a mixture of 100 vol-ppm H_2S in CO_2. The last two examples used a process gas from a hydrogen stream of a natural fat hydrodeoxygenation process. This gas contained about 560 vol-ppm H_2S in a mixture on hydrogen (93.3 vol-%), carbon monoxide, carbon dioxide, methane, ethane, propane and some butanes. Both gases were subjected at nearly atmospheric pressure to bubble through dilute $CuSO_4$ solutions. The hydrogen sulphide dissolved in the water phase and then after ionization to sulphide ions combined with Cu^{2+} ions to form practically insoluble CuS that precipitated out of the solution. The CuS precipitation happens nearly identically with both feed gases. As an additional result of the CuS precipitation sulphuric acid water solution is formed and the solution became more acidic during the tests, especially when the $CuSO_4$ concentration was 0.1 mass-% and 0.05 mass-%.

The tests clearly show that even in very dilute concentrations of Cu^{2+} ions the hydrogen sulphide can be removed from the gas by making the gas into contact with Cu^{2+} ion containing water solution. Other gases, which have been present in these tests, do not interfere.

All tests were performed in semi batch mode so that the CuSO4 solution was first prepared and then the gases were bubbled through it while the bottle was mixed. This has proved the process concept to be a working solution.

In practice, the hydrogen sulphide wash should be designed to operate in a continuous counter current multistage contacting device, like an absorption column. There the gas entering the equipment will first met solution that has little Cu^{2+} ions left and some formed CuS solid. The last contact point of the gas (only little hydrogen sulphide left) in the equipment will then be with solution that contains highest Cu^{2+} ion concentration and no CuS. The equipment can be designed so that the absorption solution is recycled. Because the solution gets acidic it will dissolve with the sulphuric acid the CuO which has been added in the solution, giving fresh Cu^{2+} ions. By proper design of the equipment it is clear based on these tests that the gas can be cleaned free of hydrogen sulphide down to ppm or sub-ppm level.

Claims

1. A method of purifying a gas stream derived from a process wherein a glyceride containing raw-material is converted to hydrocarbon paraffins, said gas stream containing a minimum of 75 vol-% of hydrogen or carbon dioxide or mixture thereof as a major component and at least one sulphide compound as an impurity, comprising the steps of:
- contacting the gas with an acidic aqueous wash solution of transition metal ions;
- binding a significant portion of the sulphide compounds contained in the gas into practically insoluble transition metal sulphide compounds; and
- separating the formed metal sulphide compounds together with the wash solution from the gas to obtain the purified gas.

2. The method according to claim 1, wherein the gas contains at least 0.1 vol-ppm of sulphide compounds.

3. The method according to claim 1 or 2, wherein the gas contains 1 vol-ppm to 1 vol-% of sulphide compounds.

4. The method according to any one of claims 1 to 3, wherein the gas contains 3 to 5000 vol-ppm of sulphide compounds.

5. The method according to any one of claims 1 to 4, wherein the sulphide compounds are selected from the group consisting of hydrogen sulphide, carbonyl sulphide, and organic sulphides.

6. The method according to any one of claims 1 to 5, wherein the gas is hydrogen-rich gas derived from a process in which the glyceride raw-material is contacted with hydrogen contains at least 80 vol.-% and up to about 99 vol.-% hydrogen.

7. The method according to any one of claims 1 to 5, wherein the gas is carbon dioxide -rich

gas which contains at least 80 vol.-% and up to about 99 vol.-% carbon dioxide.

8. The method according to any one of claims 1 to 7, wherein the gas is obtained from
- hydrogenation of fatty acids, their esters and glycerides, including mono-, di- and triglycerides;
- hydrodeoxygenation of fatty acids, their esters and glycerides, including mono-, di- and triglycerides;
- hydrocracking of fatty acids, their esters and glycerides, including mono-, di- and triglycerides; or
- from a treatment comprising a combination or two or more of the afore-going treatments; or
- the gas rich in carbon oxides is produced by a decarb reaction selected from decarboxylation and decarbonylation reactions and combinations thereof, wherein one-less-carbon n-paraffins are produced from the analogous fatty acids or carboxylic acid parts of glycerides along with carbon oxides.

9. The method according to any one of claims 1 to 8, wherein the metal ions of the wash solution are derived from transition metals selected from the group consisting of copper, zinc, iron, cobalt, and mixtures thereof.

10. The method according to any one of claims 1 to 8, wherein the metal ions of the wash solution are derived from transition metals selected from the group consisting of copper, zinc, iron, and mixtures thereof.

11. The method according to any one of claims 1 to 8, wherein the metal ions of the wash solution comprise bivalent ions of metals selected from the group consisting of copper, zinc, iron, and mixtures thereof.

12. The method according to any one of claims 1 to 11, wherein the aqueous wash solution has a pH of about 1 to about 6.5.

13. The method according to any one of claims 1 to 12, wherein the aqueous wash solution has a pH of about 1.5 to about 5.5.

14. The method according to any one of claims 1 to 13, wherein the molar ratio of the metal ion to sulphide compounds of the gas to be purified is in excess of 1.

15. The method according to any one of claims 1 to 13, wherein the molar ratio of the metal ion to sulphide compounds of the gas to be purified is about 1.4 to about 6.

16. The method according to any one of claims 1 to 13, wherein the molar ratio of the metal ion to sulphide compounds of the gas to be purified is about 1.5 to about 5.5.

17. The method according to any one of claims 1 to 13, wherein the molar ratio of the metal ion to sulphide compounds of the gas to be purified is about 2 to about 4.5.

18. The method according to any one of claims 1 to 17, wherein the wash solution contains less than 1500 wt-ppm of a metal salt.

19. The method according to any one of claims 1 to 17, wherein the wash solution contains less than 1000 wt-ppm of a metal salt.

20. The method according to any one of claims 1 to 17, wherein the wash solution contains about 10 to about 450 wt-ppm of a metal salt.

21. The method according to any one of claims 18 to 20, wherein the metal salt is a copper salt.

22. The method according to any one of claims 18 to 20, wherein the metal salt is copper sulphate.

23. The method according to any one of claims 1 to 22, wherein a significant portion of the hydrogen sulphide is removed from the gas.

24. The method according to any one of claims 1 to 23, wherein at least 95 % of the hydrogen sulphide is removed from the gas.

25. The method according to any one of claims 1 to 24, wherein at least 98 % of the hydrogen sulphide is removed from the gas.

26. The method according to any one of claims 1 to 25, wherein at least 99.5 % of the hydrogen sulphide is removed from the gas.

27. The method according to any one of claims 1 to 26, wherein the step of contacting the gas with the wash solution is preceded by at least one purification step of the gas.

28. The method according to any one of claims 1 to 27, wherein H_2S removal from the gas is carried out by washing effected in a multi-stage process.

29. The method according to claim 28, wherein the multi-stage process comprises counter-current washing.

30. The method according to claim 29, wherein the counter-current washing comprises an absorption column.

31. The method according to any one of claims 1 to 30, wherein in a first stage, the inlet gas is contacted with a washing liquid which contains less than a stoichiometric amount of metal ions with respect to the sulphide compounds present, and in a second stage of the process, the gas treated is contacted with a washing liquid which contains an excess of metal ions with respect to the sulphide compounds present in the gas.

32. The method according of any one of claims 28 to 31, wherein the washing is carried out such that the gas to be purified will first meet a solution that has a first concentration of metal ions, whereas at the last contact point between the gas and the washing solution the washing solution will have a second concentration of metal ions, said second concentration being at least 2 times greater than the first concentration.

33. The method according of any one of claims 28 to 31, wherein the washing is carried out such that the gas to be purified will first meet a solution that has a first concentration of metal ions, whereas at the last contact point between the gas and the washing solution the washing solution will have a second concentration of metal ions, said second concentration being at least 5 times greater than the first concentration.

34. The method according of any one of claims 28 to 31, wherein the washing is carried out such that the gas to be purified will first meet a solution that has a first concentration of metal ions, whereas at the last contact point between the gas and the washing solution the washing solution will have a second concentration of metal ions, said second concentration being at least 10 times greater than the first concentration.

35. The method according to any one of claims 1 to 34, wherein the gas stream comprises carbon dioxide separated from recycled hydrogen gas obtained by decarboxylation.

36. The method according to claim 35, wherein the gas stream comprising carbon dioxide is purified to produce a purified stream of carbon dioxide which is separately recovered.

37. The method according to any one of claims 1 to 34, wherein said gas stream is a stream of hydrogen gas containing carbon dioxide, said gas stream being conducted to a treatment process, wherein sulphides or other sulphur-containing compounds or combinations thereof are removed to yield a purified gas stream, and the carbon dioxide of this purified gas stream is subjected to a process for removing carbon dioxide.

38. The method according to claim 37, wherein the stream of hydrogen gas contains a maximum of 10 vol-% of carbon dioxide.

39. The method according to claim 37, wherein the stream of hydrogen gas contains 0.1 to 7.5 vol-% of carbon dioxide.

40. The method according to claim 7, wherein at least 95 % of the hydrogen sulphide is removed from the gas, to provide carbon dioxide containing less than 1 vol-ppm of hydrogen sulphide by volume.

41. The method according to claim 7, wherein at least 95 % of the hydrogen sulphide is removed from the gas, to provide carbon dioxide containing less than 500 ppb of hydrogen sulphide by volume.

42. The method according to claim 7, wherein at least 95 % of the hydrogen sulphide is removed from the gas, to provide carbon dioxide containing less than 250 ppb of hydrogen sulphide by volume.

43. The method according to claim 7, wherein at least 98 % of the hydrogen sulphide is removed from the gas, to provide carbon dioxide containing less than 1 vol-ppm of hydrogen sulphide by volume.

44. The method according to claim 7, wherein at least 98 % of the hydrogen sulphide is removed from the gas, to provide carbon dioxide containing less than 500 ppb of hydrogen sulphide by volume.

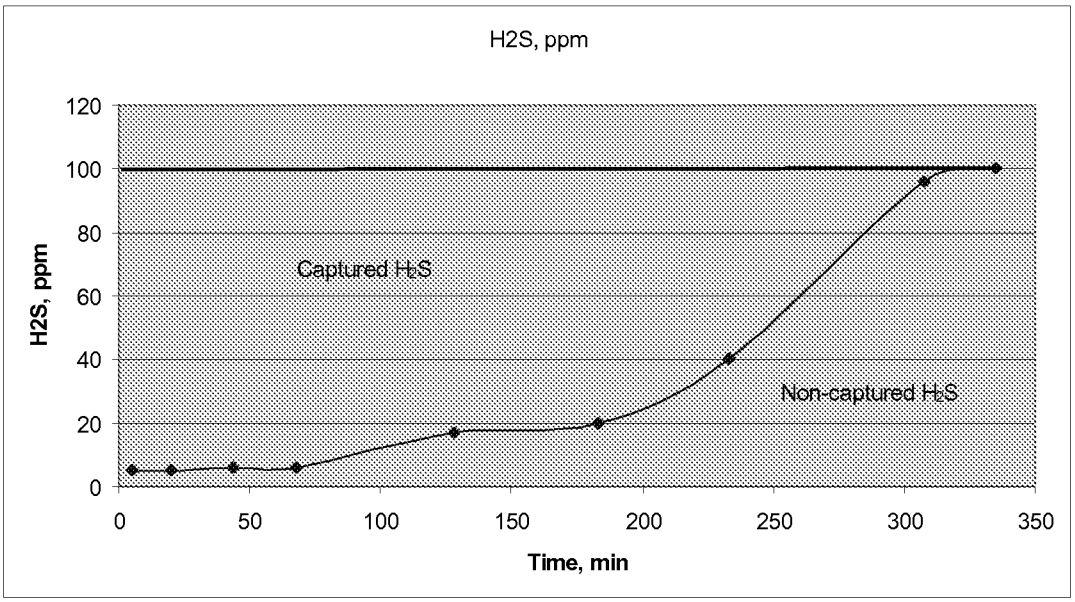
45. The method according to claim 7, wherein at least 98 % of the hydrogen sulphide is removed from the gas, to provide carbon dioxide containing less than 250 ppb of hydrogen sulphide by volume.

46. The method according to claim 7, wherein at least 99.5 % of the hydrogen sulphide is removed from the gas, to provide carbon dioxide containing less than 1 vol-ppm of hydrogen sulphide by volume.

47. The method according to claim 7, wherein at least 99.5 % of the hydrogen sulphide is removed from the gas, to provide carbon dioxide containing less than 500 ppb of hydrogen sulphide by volume.

48. The method according to claim 7, wherein at least 99.5 % of the hydrogen sulphide is removed from the gas, to provide carbon dioxide containing less than 250 ppb of hydrogen sulphide by volume.

49. A method according to any one of claims 1 to 48, wherein a glyceride containing raw-material is processed and a gas stream is treated, comprising the steps of:
- converting a glyceride containing raw-material to hydrogen paraffins;
- optionally recovering said hydrogen paraffins;
- recovering from the converting step a gas stream containing a minimum of 75 vol-% of hydrogen or carbon dioxide as a major component and at least one sulphide compound as an impurity;
- contacting the gas with an acidic aqueous wash solution of transition metal ions;
- binding a significant portion of the sulphide compounds contained in the gas into practically insoluble transition metal sulphide compounds; and
- separating the formed metal sulphide compounds together with the wash solution from the gas to obtain the purified gas.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H2S, ppm
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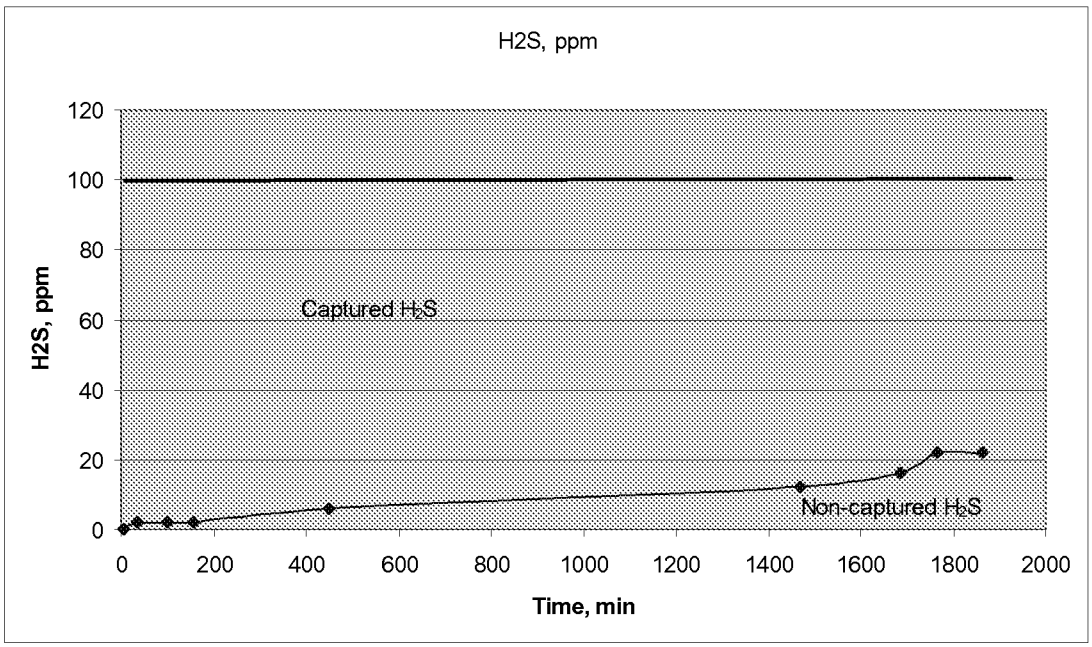
100
80
60
40
20
0
Captured H2S
Non-captured H2S
0
50
100
150
200
250
300
350
Time, min

Fig. 1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H2S, ppm
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100
80
60
40
20
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Captured H2S
Non-captured H2S
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200
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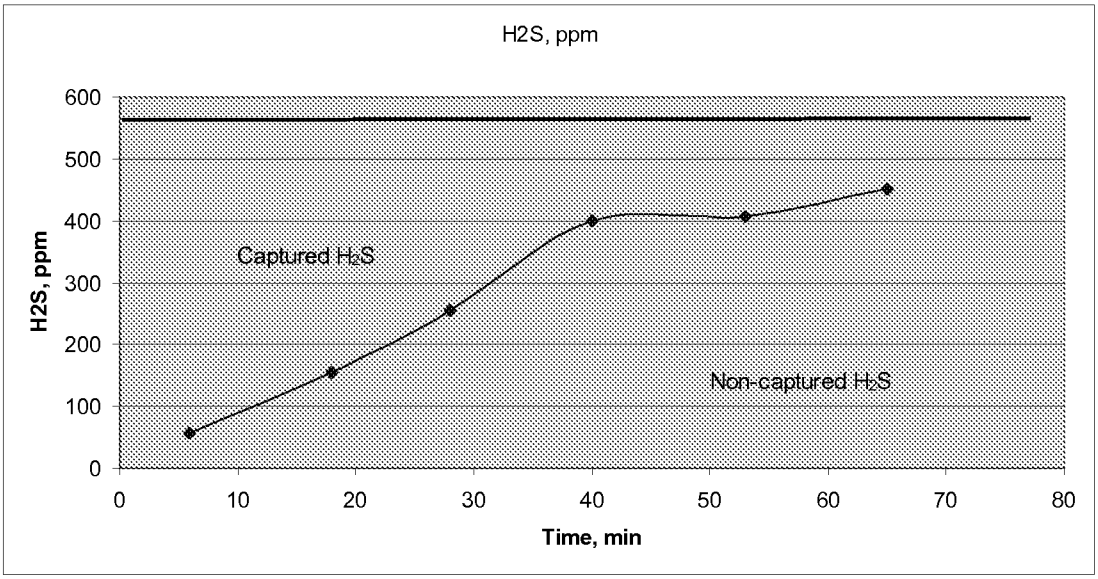
1000
1200
1400
1600
1800
2000
Time, min

Fig. 2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H2S, ppm
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500
400
300
200
100
0
Captured H2S
Non-captured H2S
0
10
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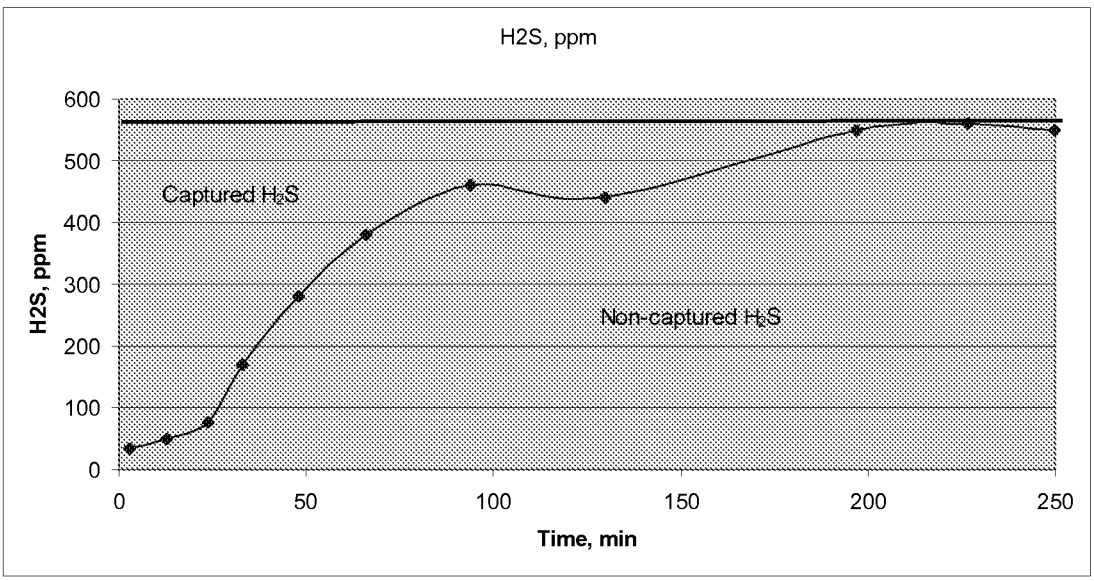
30
40
50
60
70
80
Time, min

Fig. 3


H2S, ppm
H2S, ppm
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500
400
300
200
100
0
Captured H2S
Non-captured H2S
0
50
100
150
200
250
Time, min

Fig. 4