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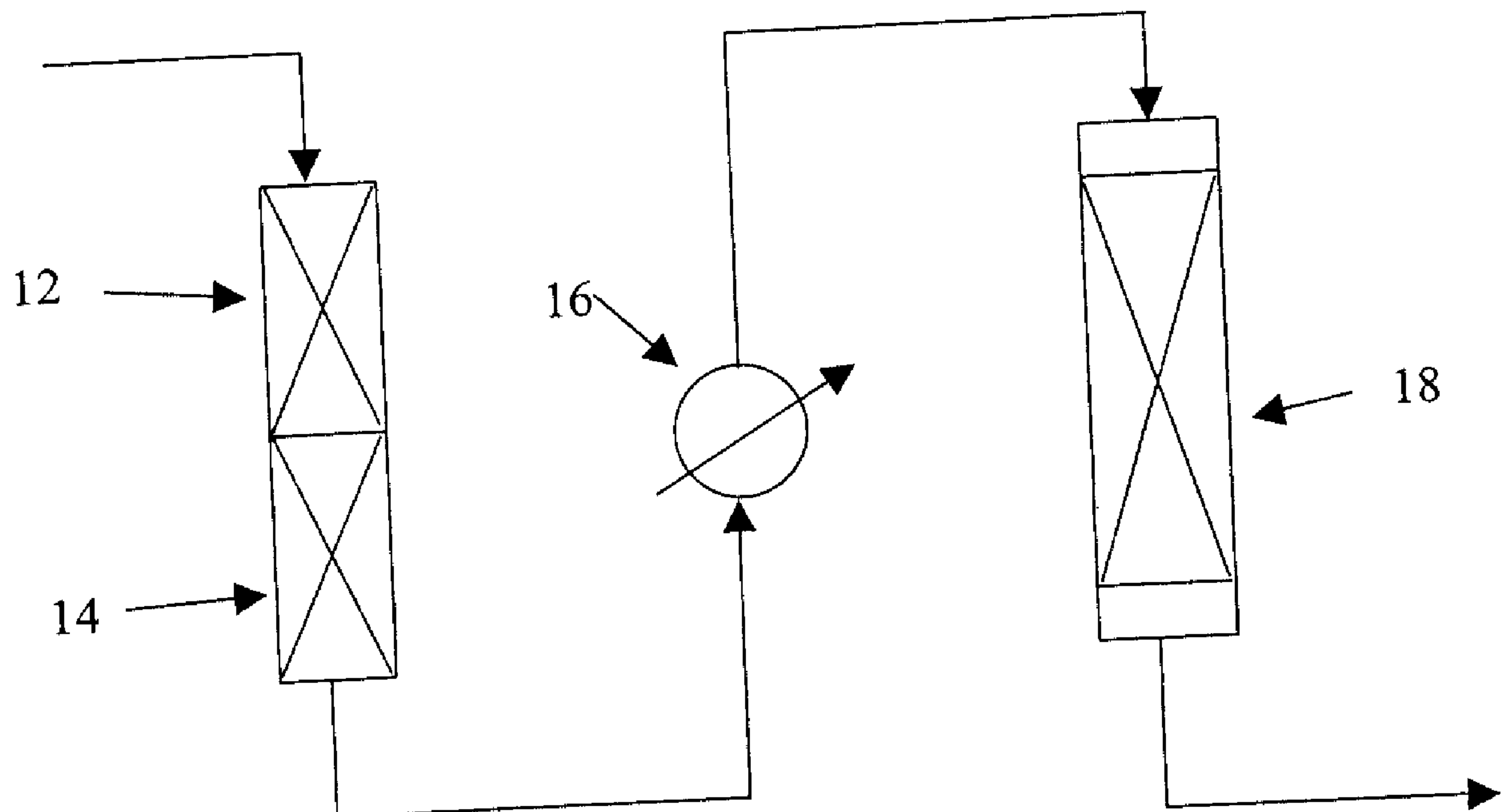
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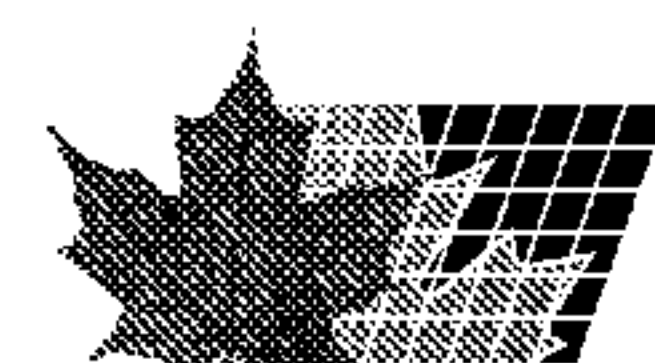
(54) Titre : METHODE DE DESULFURATION DU PROPANE

(54) Title: PROPANE DESULPHURIZATION



(57) Abrégé/Abstract:

A method of desulphurizing a hydrocarbon gas, such as propane, includes the steps of contacting the gas stream with an activated carbon or zeolite, contacting the stream with an alumina catalyst, and contacting the stream with an iron or zinc oxide at an elevated temperature.



ABSTRACT

A method of desulphurizing a hydrocarbon gas, such as propane, includes the steps of contacting the gas stream with an activated carbon or zeolite, contacting the stream with an alumina catalyst, and contacting the stream with an iron or zinc oxide at an elevated temperature.

PROPANE DESULPHURIZATION

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FIELD OF THE INVENTION

The present invention relates to a method and system for removing sulphur compounds from a gaseous hydrocarbon stream.

BACKGROUND OF THE INVENTION

10 Most fuel cell applications have a very low tolerance to sulphur compound impurities in the fuel. In the case of solid oxide fuel cells, the reforming catalyst and the anode, both of which are typically composed of nickel, are catalytically deactivated if sulphur compounds are present in greater than about 0.1 ppm. Among possible sulphurous impurities, the most common include hydrogen sulphide (H_2S), carbonyl sulphide (COS) and methyl mercaptan (CH_3SH), as well as
15 higher boiling sulphurous impurities, such as carbon disulphide (CS_2) and dimethyl sulphide (CH_3SCH_3). Many processes exist which are known to remove these sulphur compounds, including washing with chemical solutions, such as alkali and alkanolamine solutions. Removal systems using adsorption are favoured, as they are typically compact and easier to maintain. Typically, iron oxide, zinc oxide, activated carbon, etc., are utilized, but these processes have
20 inferior removal efficiency, particularly in the presence of carbonyl sulphide.

The desulphurisation of a raw fuel material prior to steam reforming is commonly carried out by hydrogenation desulphurisation in which organic sulphur in the raw fuel material is decomposed by hydrogenolysis, for example, at 350-400°C in the presence of a Ni-Mo or a Co-Mo catalyst. The resultant H_2S is then removed by adsorption on ZnO at 350-400°C. If the raw
25 fuel material contains a large amount of sulphur compounds, it is preferable to reduce their concentration by primary desulphurisation thus, minimizing consumption of the adsorption catalyst. Also, if the raw fuel material contains more stable organic sulphur compounds such as thiophene and dimethyl sulphide, it is preferable to first subject the raw fuel materials to hydrogenation desulphurisation and then, to a Zn adsorption desulphurisation agent.

Light hydrocarbon gases, such as methane, typically contain 5-10 ppm of sulphur compounds, primarily in the form of methyl mercaptan, and can easily be removed by a nickel, zeolite or carbon absorption bed. Hydrogen sulphide, the main inorganic sulphur compound, is easily removed by iron oxides or zinc oxides at moderate temperatures. From the standpoint of desulphurisation efficiency, ZnO is conventionally considered more attractive because of its higher sulphur loading capacity. The adsorption reaction between ZnO and H₂S proceeds as follows:



As this reaction does not require water to proceed, the desulphurizing apparatus does not require water or recycling equipment and can be made more compact and simple when compared to alternate approaches. However, in the presence of water, this reaction is thermodynamically driven from right to left and therefore zinc and iron oxides cannot lower the H₂S sufficiently to protect the hydrogen generation catalyst.

Heavier hydrocarbons such as propane usually contain several additional different sulphurous impurities, as well as carbon dioxide, carbon monoxide and a high water content. The concentration of these sulphur impurities in commercially available propane is typically greater than 100 ppm, with 80% consisting of carbonyl sulphide. The complexity of the impurities makes the desulphurisation of these gases exceedingly difficult. Adsorbents, such as zinc oxide, are effective in removing H₂S, but their efficiency decreases when COS and other sulphur bearing compounds are present. In particular, COS poses problems in conventional solvent-absorption schemes since it hydrolyses very inefficiently. A high concentration of water also diminishes the effectiveness of this process due to the absorbents attraction to this polar molecule. Nickel, on the other hand, is effective in removing COS and mercaptans to very low levels, but it rapidly loses its selectivity and capacity when in contact with H₂S.

Therefore, there is a need in the art for a method and apparatus for desulphurizing a propane stream which mitigates the difficulties of the prior art.

SUMMARY OF THE INVENTION

In one aspect, the invention comprises a method of desulphurizing a gaseous propane stream including water, carbon dioxide, carbon monoxide and sulphur compounds, comprising the steps of:

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- (a) contacting the stream with an activated carbon or zeolite;
- (b) contacting the stream with an alumina catalyst for hydrolyzing carbonyl sulphide to hydrogen sulphide; and
- (c) contacting the stream at an elevated temperature with zinc oxide or iron oxide

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bed.

In another aspect, the invention may comprise a reactor for desulphurizing a gaseous propane stream including water, carbon dioxide, carbon monoxide and sulphur compounds, comprising:

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- (a) a first bed comprising activated carbon or zeolite;
- (b) a second bed comprising a catalyst for hydrolyzing carbonyl sulphide to hydrogen sulphide;
- (c) a third bed comprising a metal oxide for adsorbing hydrogen sulphide; and
- (d) means for heating the third bed, or alternatively, means for heating the gas stream

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before entering the third bed.

wherein the gas stream enters the reactor into the first bed, from the first bed into the second bed and finally through the third bed before exiting the reactor. Preferably, the second bed catalyst comprises gamma alumina while the third bed metal oxide comprises zinc oxide.

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The present invention may be utilized with gaseous hydrocarbon fuels other than propane.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described by way of an exemplary embodiment with reference to the accompanying simplified, diagrammatic, not-to-scale drawings. In the drawings, Figure 1 is a schematic representation of one embodiment of the present invention.

5 **DETAILED DESCRIPTION OF THE INVENTION**

The present invention provides for a reactor and method for removing sulphur compounds from a gaseous hydrocarbon stream. When describing the present invention, all terms not defined herein have their common art-recognized meanings.

10 The invention may now be described with reference to a gaseous propane fuel. Because of the complex nature of propane, a simple solution to desulphurisation is not available. The complex interactions of the different sulphurous compounds with each other in the presence of the various adsorption beds and catalysts available reduces the desulphurisation efficiency, requiring larger catalyst beds, and thoroughness, possibly requiring further desulphurisation steps.

15 The Applicants have developed a desulphurisation process which significantly reduces the sulphur content of high mass hydrocarbons such as propane. This three-stage technique includes a two-stage low temperature desulphurisation phase, after which the fuel is further treated under elevated temperatures.

20 In one embodiment, the first stage involves activated carbon while the second stage involves γ -Al₂O₃. The activated carbon is effective at removing the majority of the mercaptan compounds, with only a small amount of H₂S adsorbed. Activated carbon is a generic term used to describe a family of carbonaceous adsorbents with a highly crystalline form and extensively developed internal pore structure. A wide variety of activated carbon products are available exhibiting markedly different characteristics depending upon the raw material and activation
25 technique used in their production. Selection of a suitable activated carbon is well within the

ability of one skilled in the art. As well, other absorbent materials such as zeolites may be suitable for this first stage.

Most of the COS is then hydrolysed on the γ -Al₂O₃ catalyst to H₂S. Due to the water impurity in propane, no hydrogen or water needs to be added and the reaction proceeds via a hydrolysis reaction as follows:



This reaction is exothermic and is therefore not favoured at elevated temperatures. Alternative catalysts may include theta-alumina or other well known catalytic materials suitable for a hydrolytic reaction.

Base catalysts, such as γ -Al₂O₃, are known to hydrolyse COS to form H₂S at temperatures above 120°C. By using a KOH and/or NaOH supported γ -Al₂O₃ structure, COS can be hydrolysed at about 50°C. Another stage is necessary in this case, however, since the COS is merely converted into H₂S. Most of the COS is converted into H₂S by catalytic hydrolysis, which is then reacted with ZnO. H₂ accelerates the conversion of COS to H₂S.

The propane containing H₂S, which has had most sulphurous compounds removed or converted to H₂S, is then directed into the final stage of elevated temperature desulphurisation. Since most of the water impurity has been used to hydrolyse the COS, the content is now low enough that it will not impede H₂S adsorption on ZnO. Using this process, sulphur-containing impurities may be reduced to below 0.1 ppm.

This process has the advantage of high sulphur removal, while minimizing the volume of catalyst that would otherwise be necessary in a single stage desulphurisation process. By maximizing the low temperature sulphur adsorption and hydrolysis (of COS), the ZnO bed required for high temperature desulphurisation is more compact, efficient and simplistic in design (i.e. no need to add H₂) and may run for a longer period of time.

In its apparatus form, the present invention comprises a desulphurizing reactor (10) shown schematically in Figure 1. Propane for use in a solid oxide fuel cell is desulphurized in a three-stage process. The fuel is first passed over an activated carbon or zeolite bed (12), which has been fabricated with standard procedures well known in the art, to remove the majority of the methyl mercaptan or similar organic sulphur compounds. The second stage of desulphurisation involves the hydrolysis of carbonyl sulphide. The γ - Al_2O_3 catalyst bed (14), prepared by standard procedures known to those skilled in the art, can be the second part of the same reactor as the activated carbon or in a vessel of its own. The fuel is then flowed through a heat exchanger (16) to heat the gas to about 350 to about 450°C and then flowed into the third stage of desulphurisation which occurs in a zinc oxide adsorbent bed (18). Alternatively, the gas stream can be heated within the adsorbent bed (18) as opposed to being heated before entering the bed. The ZnO adsorbs the H_2S with ZnS and H_2O as the end-products. Iron oxide also adsorbs H_2S and may be used in place of, or in conjunction with, ZnO. Other equivalent means of adsorbing or removing H_2S from a gas stream are well known in the art and are intended to be included within the scope of the present invention.

Once the ZnO bed (18) and activated carbon (or zeolite) bed (12) are fully infused with sulphur, they may be desulphurized using well known standard procedures.

As will be apparent to those skilled in the art, various modifications, adaptations and variations of the foregoing specific disclosure can be made without departing from the scope of the invention claimed herein. The various features and elements of the described invention may be combined in a manner different from the combinations described or claimed herein, without departing from the scope of the invention.

WHAT IS CLAIMED IS:

- 5 1. A method of desulphurizing a propane stream including water, carbon dioxide, carbon monoxide and sulphur compounds, comprising the steps of:
 - (a) contacting the stream with an activated carbon or zeolite;
 - (b) contacting the stream with an alumina catalyst for hydrolyzing carbonyl sulphide
10 to hydrogen sulphide; and
 - (c) contacting the stream at an elevated temperature with zinc oxide or iron oxide bed.
2. The method of claim 1 wherein zinc oxide is utilized and without adding hydrogen.
- 15 3. The method of claim 1 wherein step (c) is carried out without water removal.
4. The method of claim 1 wherein the catalyst of step (b) comprises gamma-alumina.
- 20 5. The method of claim 1 wherein the hydrocarbon stream comprises primarily propane.
6. A reactor for desulphurizing a propane stream including water, carbon dioxide, carbon monoxide and sulphur compounds, comprising:
 - 25 (a) a first bed comprising activated carbon or zeolite;
 - (b) a second bed comprising a catalyst for hydrolyzing carbonyl sulphide to hydrogen sulphide;
 - (c) a third bed comprising a metal oxide for adsorbing hydrogen sulphide; and
 - (d) means for heating the third bed, or alternatively, means for heating the gas stream
30 before entering the third bed.

wherein the gas stream enters the reactor into the first bed, from the first bed into the second bed and finally through the third bed before exiting the reactor.

- 5 7. The reactor of claim 6 wherein the second bed catalyst comprises gamma aluminium oxide.
8. The reactor of claim 6 wherein the third bed metal oxide comprises zinc oxide.

Figure 1

