

# UK Patent Application (12) GB (19) 2 289 286 (13) A

(43) Date of A Publication 15.11.1995

(21) Application No 9508287.1	(51) INT CL <sup>6</sup> C10L 3/10
(22) Date of Filing 24.04.1995	(52) UK CL (Edition N ) C5E EPG E181 E191
(30) Priority Data (31) 9409376 (32) 11.05.1994 (33) GB	(56) Documents Cited GB 2275625 A WO 92/20431 A1 US 5407466 A
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## (54) Removing hydrogen sulphide from gas

(57) A raw gas stream containing hydrogen sulphide, such as natural gas, is subjected to membrane separation to divide the stream into a minor permeate stream of increased hydrogen sulphide content, and a major impermeate stream of decreased hydrogen sulphide content. The permeate stream is treated with a regenerable liquid, eg methyl diethanolamine, to reduce its hydrogen sulphide content to form a first, minor, product stream. The impermeate stream is treated with a non-regenerable solid hydrogen sulphide absorbent, eg ZnO/ZnCO<sub>3</sub> to give a second, major, product stream. The first and second product streams are then combined.

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Sulphur removal

This invention relates to sulphur removal and in particular to the removal of sulphur compounds from fluid, especially gaseous hydrocarbon, streams.

Gaseous hydrocarbon streams, such as natural gas, often contain significant quantities 5 of sulphur compounds, especially hydrogen sulphide. It is generally necessary to reduce the content of the sulphur compounds to below a specified level, for example 3 vppm (ppm by volume), before the gas is supplied to customers.

A number of methods are available for removal of such sulphur compounds including:

- 10 a) treating the gas with a regenerable liquid medium that absorbs the sulphur compounds and/or converts them to elemental sulphur which can be separated;
- b) contacting the gas with a regenerable solid material such as a molecular sieve which adsorbs the sulphur compounds; and
- c) contacting the gas with a non-regenerable solid which absorbs, and usually reacts, with the sulphur compounds to form, for example, metal sulphides.

15 Which of these methods is employed will normally be determined by the nature and sulphur content of the raw gas, the desired sulphur content of the product, whether it is also desired to remove other components, such as carbon dioxide, from the gas, and the amount of gas that has to be processed. Thus where the raw gas contains only a small amount of sulphur compounds, the use of a non-regenerable solid absorbent, such as zinc and/or copper compounds, 20 is often to be preferred since the capital cost is low, the plant required is essentially maintenance-free, and the operating costs, other than the cost of replenishment of the spent absorbent, are low. The amount of absorbent required, and/or the frequency of its replenishment, increases as the amount of sulphur compounds to be removed increases. Where however the raw gas contains larger amounts of sulphur compounds, treatment with a regenerable liquid becomes 25 more economic, despite the significantly higher capital, maintenance, and running costs.

We have devised an advantageous combination of such processing techniques.

Accordingly the present invention provides a process for decreasing the sulphur content of a raw gas stream containing hydrogen sulphide, and possibly other sulphur compounds, comprising subjecting the gas stream to a membrane separation step to divide said raw gas 30 stream into a minor permeate stream having an increased hydrogen sulphide content, and a major impermeate stream having a decreased hydrogen sulphide content, subjecting the minor permeate stream to treatment with a regenerable liquid to reduce the hydrogen sulphide content of said minor permeate stream, e.g. by absorption of hydrogen sulphide and/or conversion thereof to elemental sulphur, to form a first, minor, product stream having a hydrogen sulphide content below 35 said increased hydrogen sulphide content, subjecting the major impermeate stream to treatment with a non-regenerable solid that absorbs hydrogen sulphide to give a second, major, product

stream having a hydrogen sulphide content below that of said impermeate stream, and then combining the first and second product streams.

The invention is of particular utility in the treatment of natural gas. Natural gas generally comprises a large proportion of methane and a small proportion, e.g. up to 10% by volume, of 5 higher hydrocarbons, and typically may contain minor amounts of carbon dioxide and/or nitrogen in addition to sulphur compounds, primarily hydrogen sulphide. Typically the raw natural gas has a hydrogen sulphide content in the range 5-500 vppm, and may contain smaller amounts of other sulphur compounds such as carbonyl sulphide and/or organic sulphides.

In the first stage of the process of the invention, the raw gas is subjected to a membrane 10 separation step to divide the raw gas into a permeate stream and an impermeate stream. The purpose of the membrane separation stage is to divide the raw gas into a minor permeate portion having an increased hydrogen sulphide content and a major impermeate portion having a decreased hydrogen sulphide content. Typically the permeate will amount to about 5-40% of the total feed to the membrane separation stage and will typically contain about 50-95% of the 15 hydrogen sulphide in the raw gas feed, while the impermeate correspondingly amounts to 60-95% of the raw gas feed but contains only 5-50% of the hydrogen sulphide therein. Preferably the impermeate will have a hydrogen sulphide content of less than 15 vppm. The membrane separation stage does not have to be particularly selective: thus the permeate will contain other components of the raw gas as well as hydrogen sulphide. Thus where the raw gas is natural gas, 20 the permeate will generally contain methane, carbon dioxide, and may also contain nitrogen, carbonyl sulphide, and/or organic sulphur compounds as well as hydrogen sulphide. The permeate stream will generally contain a substantial proportion of any water vapour that was in the raw gas stream. Where the raw gas is natural gas, the impermeate stream will generally contain the remainder of the methane, the bulk of the higher hydrocarbons present in the raw gas, and 25 some hydrogen sulphide and possibly also carbonyl sulphide and/or organic sulphur compounds. It may also contain nitrogen, carbon dioxide, and water vapour.

Membrane materials that may be employed are generally polymeric materials such as polysulphones, cellulose acetate, polyimides, polycarbonates, polyamides, polyetherimides and sulphonated polysulphones. The temperature at which the membrane separation step is operated 30 will normally be limited by the nature of the membrane: preferably the temperature is below about 90°C. The pressure of the feed to the membrane separation step will usually be in the range 10-100 bar abs. The composition of the permeate will generally depend on the nature of the membrane material and on the temperature and pressures employed. The use of conditions where the permeate contains the bulk of the carbon dioxide in the raw gas is useful where it is 35 desired to decrease the carbon dioxide content as well as the sulphur compounds content of the raw gas, since it is possible to select a regenerable liquid treatment stage that effects separation of

carbon dioxide as well as hydrogen sulphide. Another factor affecting the selection of the nature of the membrane and the membrane separation step operating conditions is the ability of the subsequent regenerable liquid treatment step to handle gases containing carbonyl sulphide and/or organic sulphur compounds. Thus where such compounds might interfere with the subsequent 5 regenerable liquid treatment step, it may be preferably to employ a membrane separation stage where such compounds do not pass, to any significant extent, into the permeate. Alternatively it may be desirable in some cases to subject the permeate to a hydro- desulphurisation stage before the regenerable liquid treatment stage.

The regenerable liquid treatment stage may be any of those commonly employed, e.g. 10 involving contacting the gas with a suitable liquid such as sulpholane, propylene carbonate, poly(ethylene glycol) dimethyl ether, or a solution of one or more amines such as monoethanolamine, diethanolamine, methyl-diethanolamine, diisopropanolamine, to form an absorbent solution loaded with hydrogen sulphide. Depending on the nature of the liquid absorbent employed, any carbon dioxide in the permeate stream may also be absorbed. The 15 loaded absorbent liquid is then subjected to a regeneration process, which generally involves reduction in pressure and/or heating to desorb the hydrogen sulphide, and any absorbed carbon dioxide, which is recovered. The regenerated absorbent liquid is then recycled.

The present invention, involving a membrane separation step to form a gas stream that in which the hydrogen sulphide is more concentrated, enables the size of the plant required for the 20 regenerable liquid treatment stage to be reduced. Furthermore, since some of the absorbent liquids may absorb higher hydrocarbons, the use of a membrane separation step whereby such higher hydrocarbons are separated into the impermeate stream and so are not present in any substantial proportion in the permeate stream, avoids the loss of such higher hydrocarbons.

Alternatively there may be used liquid treatment systems wherein the permeate gas is 25 absorbed by contact with a solution containing a polyvalent metal compounds, often an iron compound, and a chelating agent. The loaded absorbent is then regenerated by subjecting it to oxidation conditions effecting the production of elemental sulphur which is separated and the regenerated solution is recycled.

Depending on the nature of the regenerable liquid and the conditions employed, this 30 stage may also remove carbonyl sulphide and/or organic sulphur compounds present in the permeate stream.

It is not necessary that the regenerable liquid treatment stage effects complete removal of the hydrogen sulphide in the permeate. Indeed, since the permeate stream is only a minor proportion of the raw feed gas, it is not necessary that the hydrogen sulphide content of the first 35 product stream resulting from the regenerable liquid treatment stage is below that of the raw gas.

The impermeate stream is subjected to treatment with a solid non-regenerable absorbent. Normally this is effected by passing the impermeate stream through a fixed bed of particles, e.g. granules or pellets of the solid, non-regenerable absorbent. The solid non-regenerable absorbent may be any of those conventionally employed for desulphurisation, 5 and will normally comprise one or more metals, or compounds thereof, selected from zinc, copper, nickel, iron, manganese, tin, lead, and silver. Other metals or compounds thereof may also be present. The particulate absorbent preferable comprises zinc compounds, such as zinc oxide, zinc carbonate, zinc hydroxycarbonate, and mixtures thereof, alone or in conjunction with other metals or compounds thereof, such as copper, copper oxide, copper carbonate, basic copper carbonate, 10 alumina and/or calcium aluminate.

The temperature employed for the treatment with the solid, non-regenerable, absorbent will depend on the absorbent employed and typically will be in the range 0-400°C, particularly 0-100°C.

Depending on the nature of the solid, non-regenerable absorbent and the conditions 15 employed, this stage may also remove carbonyl sulphide and/or organic sulphur compounds present in the impermeate stream.

Typically the second product stream, i.e. the effluent from the solid, non-regenerable, absorbent treatment stage, has a hydrogen sulphide content below 1 vppm and is then mixed with the first product stream, i.e. the product from the regenerable liquid treatment stage.

20 Since the hydrogen sulphide content of the mixture of the first and second products may be significantly below the maximum permitted by the final product specification, it may be possible to provide for part of the raw gas, and/or part of the impermeate, to bypass subsequent treatment stages and be blended directly with the first and second product streams to give a final product still satisfying the final product specification.

25 As an example of the invention, natural gas of volume composition methane 89%, ethane 7%, propane 1%, nitrogen 1%, and carbon dioxide 2% and containing 38 vppm of hydrogen sulphide is fed to a membrane separation unit at 65°C and 73 bar abs. pressure and at a flow rate of 700 MMSCFD (36900 kmol/h) to give a permeate having the approximate volume composition methane 86.5%, ethane 5.9%, propane 0.1%, nitrogen 1%, carbon dioxide 6.5% and 30 containing 117 vppm of hydrogen sulphide at about 2 bar abs. pressure at a rate of 206 MMSCFD (10900 kmol/h) and an impermeate stream of approximate volume composition methane 90%, ethane 7.5%, propane 1.4%, and containing 5 vppm of hydrogen sulphide. The flow rate of the permeate stream is thus about 29% of the total feed rate.

The permeate stream is then subjected to an amine wash stage using methyl 35 diethanolamine as a regenerable liquid absorbent to remove hydrogen sulphide therefrom to give a first product stream containing about 5 vppm of hydrogen sulphide.

The impermeate stream is then passed at 45°C through a 80 m<sup>3</sup> bed of granules of a zinc oxide/carbonate absorbent to give a second product stream containing less than 1 vppm of hydrogen sulphide.

Mixing the first and second product streams gives a final product at about 50 bar abs.

5 containing about 2 ppm of hydrogen sulphide. Where it is desired that the product is delivered at a pressure greater than that resulting simply from mixing the first and second products, the permeate stream may be compressed before or after the amine wash.

Where compression is necessary and a source of power is not available, a gas turbine may be installed to drive the compressor with the gas turbine fuelled by a portion of one of the gas

10 streams, preferably a portion of the raw gas stream or of the permeate gas stream, before or after the treatment thereof with the regenerable liquid.

It is seen that about 87% of the hydrogen sulphide is removed by the amine wash step yet the gas flow rate therethrough is only 29% of the feed gas flow rate. The solid, non-regenerable, absorbent removes about 7.5% of the hydrogen sulphide.

Claims

1. A process for decreasing the sulphur content of a raw gas stream containing hydrogen sulphide comprising subjecting the gas stream to a membrane separation step to divide said raw gas stream into a minor permeate stream having an increased hydrogen sulphide content, and a major impermeate stream having a decreased hydrogen sulphide content, subjecting the minor permeate stream to treatment with a regenerable liquid to reduce the hydrogen sulphide content of said minor permeate stream to form a first, minor, product stream having a hydrogen sulphide content below said increased hydrogen sulphide content, subjecting the major impermeate stream to treatment with a non-regenerable solid that absorbs hydrogen sulphide to give a second, major, product stream having a hydrogen sulphide content below that of said impermeate stream, and then combining the first and second product streams.
2. A process according to claim 1 wherein the permeate stream constitutes 5-40% of the total feed to the membrane separation stage and, before the treatment with the regenerable liquid, contains about 50-95% of the hydrogen sulphide in the raw gas feed, while the impermeate stream correspondingly constitutes 60-95% of the raw gas feed and, before the treatment with the non-regenerable absorbent, contains 5-50% of the hydrogen sulphide therein.
3. A process according to claim 1 or claim 2 wherein, before the treatment with the non-regenerable absorbent, the impermeate has a hydrogen sulphide content of less than 15 vppm.
4. A process according to any one of claims 1 to 3 wherein the membrane separation step is effected at a temperature below 90°C.
5. A process according to any one of claims 1 to 4 wherein the membrane separation step is such that carbonyl sulphide and organic sulphur compounds present in the raw gas feed do not pass into the permeate.
6. A process according to any one of claims 1 to 4 wherein the permeate is subjected to a hydrodesulphurisation stage before treatment with the regenerable liquid.
7. A process according to any one of claims 1 to 6 wherein the solid non-regenerable absorbent comprises one or more metals, or compounds thereof, selected from zinc, copper, nickel, iron, manganese, tin, lead, and silver.

8. A process according to claim 7 wherein the solid non-regenerable absorbent comprises zinc compounds selected from zinc oxide, zinc carbonate, zinc hydroxycarbonate, and mixtures thereof, alone or in conjunction with copper, copper oxide, copper carbonate, basic copper carbonate, alumina and/or calcium aluminate.
9. A process according to any one of claims 1 to 8 wherein the impermeate is treated with the non-regenerable absorbent at a temperature in the range 0-100°C.

Relevant Technical Fields

(i) UK Cl (Ed.N) C5E (EPG); B1L (LEA)  
 (ii) Int Cl (Ed.6) C10L (3/06, 08, 10, 12)

Search Examiner  
R E HARDY

Date of completion of Search  
30 JUNE 1995

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-  
ALL

(ii) WPI, CLAIMS

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Category	Identity of document and relevant passages		Relevant to claim(s)
A	GB 2275625 A	(SHELL) whole document	1
A,P	US 5407466 A	(LOKHANDWALA) column 20 line 51 onwards	1
A	WO 92/20431 A	(EXXON) whole document	1

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