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WO-A1-03/014015
US-A- 3 534 528
US-A- 5 556 449
US-B1- 7 060 233

DESCRIPTION

[0001] The present invention relates to a method for removing hydrogen sulfide from an acid gas. More specifically, a stream of acid gas containing hydrogen sulfide (H_2S) and carbon dioxide (CO_2) is removed from a hydrocarbon-containing gas, such as natural gas, associated gas or biogas, and subjected to a treatment to remove H_2S involving a novel use of certain known catalysts in combination with membrane separation technology, as will be specified in the following.

[0002] Although the terms "acid gas" and "sour gas" are sometimes used interchangeably, a sour gas is any gas that specifically contains H_2S in significant amounts, whereas an acid gas is any gas that contains significant amounts of acidic gases such as CO_2 and H_2S . For bulk removal of CO_2 and H_2S at off-shore platforms, membrane technology is often used. Bulk removal of sour gas has certain advantages with respect to pipeline transport of the gas to shore. When the membrane unit is in operation, increasing the operation temperature leads to a lower throughput and allows a certain slip of hydrocarbons to the permeate side of the membrane. In practice, this means that the CO_2 and H_2S containing stream can be flared on the platform, whereby H_2S is converted to SO_2 in a thermal process. However, flaring implies loss of a valuable product that could instead have been transported to shore and sold.

[0003] A common method for the abatement of H_2S has so far been elimination by thermal incineration and catalytic oxidation. The thermal incineration is costly, as it requires the addition of a support fuel and incineration at temperatures above $800^\circ C$, whereas prior art catalytic oxidation has been in the presence of a catalytic material comprising a noble metal, typically with the oxidation of H_2S taking place at a temperature above $280^\circ C$. Such catalytic oxidation may thus also require support heating.

[0004] The oxidation of H_2S could in principle be performed in a regenerative thermal oxidizer (RTO), which would require less fuel compared to non-regenerative thermal oxidation, i.e. flaring. However, RTOs are too large and heavy to be applicable on off-shore platforms. Moreover, the thermal process requires a temperature of between 800 and $1200^\circ C$ depending on the gas composition and the slip allowed, so this *in situ* oxidation of H_2S in a regenerative thermal oxidizer is not an attractive option.

[0005] It has now turned out that it is possible to carry out the H_2S oxidation on the offshore platform by using a combination of membrane separation technology and a certain group of catalysts which are known per se, albeit for other purposes.

[0006] The removal of acid gas from hydrocarbon gas mixtures by selective absorption in a gas separation unit offshore is described in WO 2013/082242. The acid gas components are adsorbed on a sterically hindered amino ether sorbent. The process is capable of removing

H₂S from gas mixtures which also contain CO₂ in addition to the hydrocarbon components. Furthermore it is known to use various technologies to remove H₂S and CO₂ on offshore platforms. Thus, a system for the removal of H₂S and CO₂ from natural gas via absorption and disassociation utilizing counter-current scrubbers and a seawater contact system is described in US 2004/0057886, and specific membrane reactors for gas separation are known from e.g. US 2007/0240565, which describes a system for selective removal of CO₂, H₂S and H₂ from a gaseous fluid mixture, the system comprising three consecutive membrane sections, one for each species to be removed.

[0007] US3534528 discloses the removal of hydrogen sulphide from natural gas by membrane permeation.

[0008] Catalysts and catalytic processes for selective oxidation of H₂S are i.a. known from US 6,099,819 which describes catalysts for the partial oxidation of H₂S to elemental S and H₂O, the catalytically active component being TiO₂ in mixture with one or more metal oxides of transition metals or lanthanide metals. A multistage oxygen-added catalytic partial oxidation process and apparatus for converting H₂S in an acid gas stream to elemental S and H₂O are disclosed in US 7,108,842; the most preferred catalyst is a Pt-Rh alloy containing an alkaline element and/or one or more lanthanide elements.

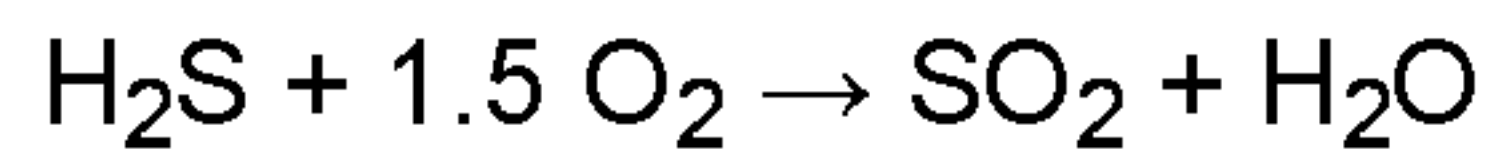
[0009] US 2012/0251436 describes processes for sulfur recovery from H₂S-containing gases using catalytic conversion of H₂S to elemental S on a solid catalyst, especially an iron-zinc oxide catalyst, in a fixed-bed oxidation reactor followed by a Claus reaction. The selective oxidation of H₂S to elemental sulfur on vanadium-based catalysts containing Sn and Sb is described in Ind. Eng. Chem. Res. 40, p. 1052-1057 (2001).

[0010] The present invention concerns the use of certain known catalysts in combination with established membrane separation technology, said combination being novel and making it possible to remove H₂S at off-shore platforms without having to flare the acid gas on site.

[0011] The invention is a method according to claim 1.

[0012] The method according to the invention comprises the steps of:

- feeding the gas to a membrane separation unit, optionally after membrane pre-treatment, drying and/or extraction of higher hydrocarbons (i.e. hydrocarbons having a higher molecular weight than methane),
- collecting the product gas from the membrane unit,
- heating the permeate stream to the necessary inlet temperature for catalytic oxidation of H₂S, and
- feeding the heated permeate stream to a catalytic oxidation unit, where H₂S is oxidized to SO₂ according to the equation



wherein the heating of the permeate stream is accomplished by using a fraction of the feed gas to heat the permeate stream in a separate heater. An alternative to pre-heating the permeate stream is to use a steam-fired heater.

[0013] The hydrocarbon-containing gas to be fed to the membrane separation unit is natural gas, e.g. associated gas or biogas. Associated gas is a form of natural gas, which is found with deposits of petroleum, either dissolved in the oil or as a free "gas-cap" above the oil in the reservoir. Due to the remote location of many oil fields, either at sea or on land, associated gas is usually burnt off in gas flares instead of being exploited.

[0014] The catalyst to be used in the catalytic oxidation unit is a monolithic metal oxide catalyst consisting of one or more metal oxides. The metal is taken from the group comprising V, Cr, W, Ce, Mo, Nb, Fe, Si, Ti, Al, Ca and Mg, and one or more supports taken from the group comprising Al_2O_3 , SiO_2 , SiC and TiO_2 , optionally in the presence of other elements in a concentration below 1 wt%.

[0015] A monolithic, catalytically active material (or a catalyst monolith) is a specific physical configuration of a catalyst, in which a structural substrate (with little or no contact with the reacting gas) is covered by a porous support, on which the active material is deposited.

[0016] The invention is illustrated further by the following example showing the advantages of the method of the invention over the prior art.

Example

[0017] A nominal gas feed stream is supplied in an amount of 400,000 Nm^3/h at a pressure of 25 bar gauge and a temperature of 30°C. This gas feed stream has the following composition: 39 % CO_2 , 1.5 % N_2 , 44.6 % methane, 6.8 % ethane, 4.9 % propane, 1 % butane, 0.3 % pentane and 1.9 % higher hydrocarbons (C_{5+}).

[0018] The gas feed stream is passed through a membrane separation unit, resulting in a product gas stream which may contain 22 % CO_2 and 50 ppm H_2S . A normal membrane pre-treatment, drying, extra compression and extraction of natural gas liquids may have been applied.

[0019] The permeate stream is in an amount of around 70,000 Nm^3/h CO_2 with around 28 ppm H_2S . It exits the membrane separation unit at a pressure close to ambient pressure.

[0020] In order to thermally oxidize the H_2S , a temperature of 700-900°C is needed. The exact lower temperature limit for the membrane operation is set by the hydrate formation temperature, but it is often in the range of 10-20°C. In the case of using a thermal oxidation process, an equivalent of 30-35 MW will be needed for this CO_2 dominated stream to reach a temperature of 800°C. This corresponds to approximately 100 MM BTU/h or - with a gas price of 10 US\$ per MM BTU - to approximately 3.5 MM US\$ per year or around 3000 Nm^3/h natural gas for flaring the permeate stream.

[0021] There are two ways of providing the fuel needed for the flare:

- to operate the membrane at a higher temperature and let fuel slip to the permeate side through the membrane, or
- to route dedicated fuel to the flare.

[0022] Both methods are employed in practice.

[0023] In contrast, a catalytic oxidation unit of the type used in the method of the invention will require an inlet temperature of 250°C and 9 MW or 870 Nm^3/h of fuel. This will represent a fuel saving of 2.5 MM US\$ per year. In this case, the membrane should operate as cold as possible without any risk of hydrate formation, and the necessary fuel is to be routed directly to a pre-heat burner to heat the inlet of the catalytic oxidation unit. Other heat sources, such as steam, may also be used to pre-heat the feed gas stream to the catalytic oxidation unit.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO2013082242A [0006]
- US20040057886A [0006]
- US20070240565A [0006]
- US3534528A [0007]
- US6099819A [0008]

- US7108842B [0008]
- US20120251436A [0009]

Non-patent literature cited in the description

- Ind. Eng. Chem. Res., 2001, vol. 40, 1052-1057 [0009]

Patentkrav:

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1. Fremgangsmåde til fjernelse af hydrogensulfid (H₂S) fra naturgas, hvilken fremgangsmåde omfatter følgende trin:

10 - tilførsel af gassen til en membranseparationsenhed, eventuelt efter membranforbehandling, tørring og/eller ekstrahering af højere carbonhydrider,

- opsamling af produktgassen fra membranenheten,

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- opvarmning af permeatstrømmen til den nødvendige indløbstemperatur for katalytisk oxidation af H₂S, og

- tilførsel af den opvarmede permeatstrøm til en katalytisk
20 oxidationsenhed, hvor H₂S oxideres til SO₂ i henhold til ligningen



25 hvor

- membranseparationsenheden og den katalytiske oxidationsenhed er placeret på et offshore-anlæg,

30 - opvarmningen af permeatstrømmen opnås enten under anvendelse af en fraktion af tilførselsgassen til opvarmning af

permeatstrømmen i et separat varmeaggregat eller under anvendelse af et dampfyret varmeaggregat,

5 - katalysatoren, der skal anvendes i den katalytiske oxidationsenhed, er en monolitisk metaloxidkatalysator, som består af et eller flere metaloxider, og

10 - metallet i katalysatorens metaloxid vælges fra gruppen, der omfatter V, Cr, W, Ce, Mo, Nb, Fe, Si, Ti, Al, Ca og Mg og et eller flere bærestoffer taget fra gruppen, der omfatter Al_2O_3 , SiO_2 , SiC og TiO_2 .

15 2. Fremgangsmåde ifølge krav 1, hvor naturgassen er biogas.

3. Fremgangsmåde ifølge krav 1, hvor naturgassen er associeret gas.

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4. Fremgangsmåde ifølge krav 1, hvor permeatforopvarmningstemperaturen ligger i temperaturområdet 180-400 °C.

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5. Fremgangsmåde ifølge krav 4, hvor permeatforopvarmningstemperaturen ligger i temperaturområdet 220-350 °C.

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