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(54) Title: A METHOD FOR THE REMOVAL OF OXYGEN FROM AN INDUSTRIAL GAS

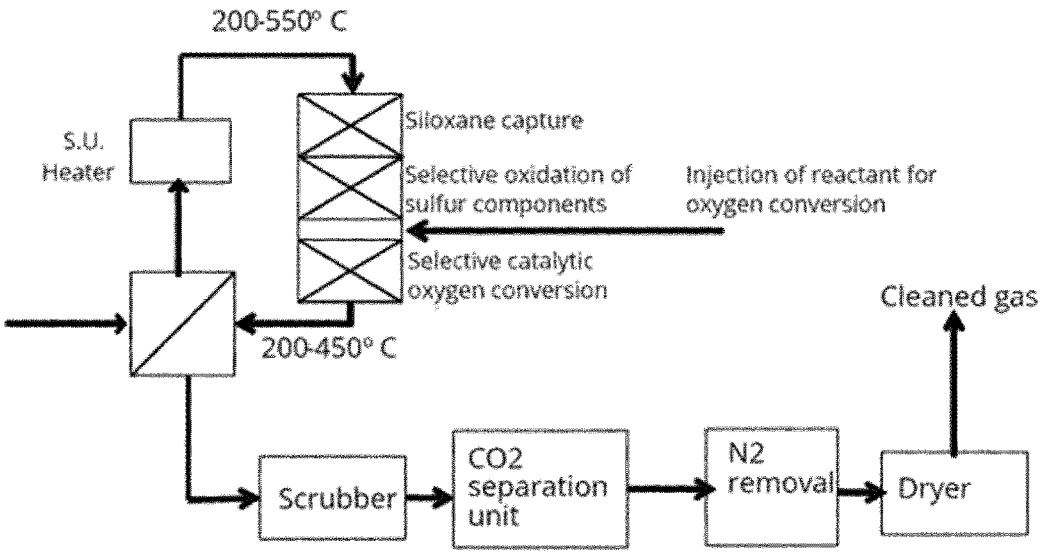

Fig. 1

(57) Abstract: Oxygen is removed from a gas feed such as a landfill gas, a digester gas or an industrial CO_2 off-gas by removing sulfur-containing compounds and siloxanes from the feed gas, heating the feed gas, optionally removing siloxanes and silanols from the heated feed gas, optionally removing part of the sulfur-containing compounds in the heated feed gas, optionally converting any or all of the volatile organic compounds (VOCs) present in the gas, including sulfur-containing compounds and/or chlorine-containing compounds, in the heated feed gas, injecting one or more reactants for oxygen conversion into the heated feed gas, carrying out a selective catalytic oxygen conversion in at least one suitable reactor, and cleaning the resulting oxygen-depleted gas. The reactants to be injected comprise one or more of H_2, CO, ammonia, urea, methanol, ethanol and dimethyl ether (DME).

[Continued on next page]

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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
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A method for the removal of oxygen from an industrial gas

The present invention relates to a novel method for the removal of oxygen from an industrial gas through selective catalytic oxidation via reactant injection.

More specifically, the invention concerns an alternative route to reduce the oxygen content in industrial gases, where the reduction of the content of oxygen is crucial for the valorization of the gas. The method of the invention is especially focused on siloxane/silanol removal and/or sulfur conversion/removal taking place in the hot loop rather than before it.

The method of the invention is focusing on landfill gas, digester gas and industrial CO_2 off-gas. Today, oxygen removal is accomplished through PSA (pressure swing adsorption), membrane or scrubber technologies with very high capital expenditure (CAPEX) and also a substantial loss of valuable components, such as methane in the main gas to the oxygen-containing off-gas. The present invention comprises addition of components, such as H_2, CO, methanol, ammonia or ethanol, to the main gas stream and leading the resultant gas stream to at least one catalytic reactor. In said reactor(s), the oxygen is converted selectively to CO_2 and water across the catalyst.

Removal of oxygen from fuel gas streams is often a requirement for distribution of the gas in the natural gas grid, and it is also a requirement when utilizing the gas as a vehicle transportation fuel. In addition, removal of oxygen is also critical for the utilization of other industrial

gas streams, such as in producing merchant or industrial grade CO_2 from oxygen-containing off-gases.

US 3.361.531 describes the removal of oxygen from oxygen-containing environments and gas mixtures by absorption in a solid material contact mass. More specifically, a compound selected from copper carbonate, manganese carbonate and iron carbonate is contacted with a hydrogen-containing gas at an elevated temperature below about 500°C, thereby reducing the carbonate to the corresponding oxide compound. This oxide compound is brought into contact with said oxygen-containing environment at around ambient temperature, thereby absorbing the oxygen and oxidizing the oxide compound.

US 2013/0209338 A1 discloses an integrated cleaning system to clean biogas from sources such as landfills and digesters for heat and power generation systems. Siloxanes, chlorine, oxygen and sulfur are removed to ppb levels, and the majority of water and some VOCs is removed as well. The system cools a biogas stream to partially remove contaminants, blends in a small concentration of hydrogen gas and then combusts the remaining oxygen to heat the biogas and leave sufficient hydrogen suitable for a downstream sequence of further contaminant conversion and removal in stages using a hydrodesulfurization bed and adsorbent media beds. This may well be a reasonable approach for low sulfur levels, but not when the H_2S level exceeds 200-300 ppm. The approach according to the present invention is different in that methanol or other reducing agents can be used, and the impurities are kept in oxidized form to be removable from the stream by using a scrubber.

The technologies dominating the industry today are PSA and membrane based technologies in small and medium sized projects (typically up to 10,000 Nm^3/h gas), whereas distillation and cryogenic separation are dominating in larger scale applications.

For applications in the digester gas and landfill gas purification industry the gas flows are in the range of 500 to 10,000 Nm^3/h, and technologies based on PSA and membranes are dominating. Apart from an often prohibitive CAPEX, PSA and membrane technologies have a high operation cost because of their complexity and gas compression as well as a substantial loss of valuable hydrocarbons, such as methane, from the feed gas stream to the oxygen-containing waste gas stream.

In the method according to the present invention, one or more components suitable for catalytic oxidation are injected into the oxygen-containing main gas stream after removal of sulfur-containing compounds and siloxanes from the gas. The components and the catalyst are chosen so that the catalyst oxidizes the injected components using the oxygen in the stream without substantially oxidizing the valuable components, such as methane, in the gas stream.

The components to be injected may comprise one or more of i.a. H_2, CO, ammonia, urea, ethanol and dimethyl ether (DME).

The active catalyst may comprise a metal selected among vanadium, tungsten, chromium, copper, manganese, molybdenum,

platinum, palladium, rhodium and ruthenium in metallic or metal oxide form supported on a carrier selected from alumina, titania, silica and ceria and combinations thereof.

Sulfur impurities in an industrial gas can create a corrosive environment inside power generating equipment or even poison catalysts that may be present. In addition, hydrogen sulfide present in the feed gas to gas engines will cause degradation of the lubricating oil and lead to a need of frequent maintenance. Furthermore, H_2S needs to be removed if the gas is to be sent to gas pipelines or used as fuel in vehicles.

Another reason to clean the gas is that other impurities, such as siloxanes, can be deposited within heat and power generation equipment and cause significant damage to the internal components.

Siloxanes are organosilicon compounds comprising silicon, carbon, hydrogen and oxygen which have Si-O-Si bonds. Siloxanes can be linear as well as cyclic. They may be present in digester or landfill gas because they are used in various beauty products, such as e.g. cosmetics and shampoos that are washed down drains or otherwise disposed of, so that they end up in municipal wastewater and landfills. Siloxanes are not broken down during anaerobic digestion, and as a result, waste gas captured from treatment plants and landfills is often heavily contaminated with these compounds. It is known that siloxanes can be removed using non-regenerative packed bed adsorption with activated carbon or porous silica as sorbent. Regenerative sorbents can also be used as well as units based on gas cooling to very

low temperatures to precipitate the siloxanes out from the gas. Further, liquid extraction technologies are used. In addition, these technologies can be used in combination.

A silanol is a functional group in silicon chemistry with the connectivity Si-O-H. It is related to the hydroxy functional group C-O-H found in all alcohols.

So a major issue in the utilization of raw gas from landfills and anaerobic digesters is to provide a gas stream with a low sulfur content, i.e. less than a few hundred ppm, and with a very low content of siloxanes, typically linear or cyclic dimethyl Si-O-Si compounds, and silanols. Pipeline specifications for natural gas are even stricter. In this case, H_2S must be removed to a residual concentration below 5 ppm, and CO_2 and N_2 need to be removed as well. Combustion of sulfur containing compounds leads to formation of sulfur trioxide which will react with moisture in the gas to form sulfuric acid, which can condense in cold spots and lead to corrosion. However, particularly siloxanes give rise to problems because they are converted to SiO_2 during combustion, leading to build-up of abrasive solid deposits inside the engine and causing damage, reduced service time and increased maintenance requirements for many components such as compressors, fans, blowers, burner nozzles, heat recovery surfaces in boilers and for gas engine components such as spark plugs, valves, pistons etc. In addition to causing damage and reduced service time to the engine, also any catalysts installed to control exhaust gas emissions are sensitive to SiO_2 entrained in the gas stream, in fact even more so than the engine itself.

For an SCR (selective catalytic reduction) catalyst, for example, the SiO_2 tolerance can be as low as 250 ppb.

For the reasons outlined above it is very desirable to remove siloxanes, silanols and sulfur-containing compounds from gas streams.

Thus, the present invention relates to a method for the removal of oxygen from an industrial gas feed, said process comprising the steps of:

(a) heating the feed gas,

(b) optionally removing siloxanes and silanols from the heated feed gas,

(c) optionally removing part of the sulfur-containing compounds in the heated feed gas,

(d) optionally converting any or all of the volatile organic compounds (VOCs) present in the gas, including sulfur-containing compounds and/or chlorine-containing compounds, in the heated feed gas,

(e) injecting one or more reactants for oxygen conversion into the heated feed gas,

(f) carrying out a selective catalytic oxygen conversion in at least one suitable reactor, and

(g) cleaning the resulting oxygen-depleted gas.

Preferably the gas feed, from which oxygen is to be removed, is a landfill gas, a digester gas or an industrial CO_2 off-gas.

In a preferred embodiment of the method of the invention, a gas stream, such as a landfill gas containing H_2S and organic sulfur along with siloxanes, CO_2, H_2O, methane and various VOCs (volatile organic carbon compounds), is treated.

The components to be injected in step (d) comprise one or more of H_2, CO, ammonia, urea, methanol, ethanol and dimethyl ether (DME).

Landfill gas of low quality, i.e. having a high content of nitrogen and oxygen, is more difficult and expensive to upgrade to pipeline quality than gases with a lower content of nitrogen and oxygen. Using the reactant injection to remove the oxygen from low quality landfill gases will lead to a high temperature increase in the reactor, which in turn will damage the catalyst. If, however, the reactant is dosed at two different points instead of one point, it is possible to use two reactors in series with cooling and reactant injection in between. This approach has the added benefit that the energy recovered after each reactor can be used in a reboiler in the CO_2 separation unit (amine wash) to regenerate the amine, and it can also be used as a feed preheater. The energy for the reboiler and for preheating of the feed would otherwise have to come from electricity or from combustion of landfill gas or natural gas.

The heat coming from the oxidation can be transferred to an oil or steam circuit which is used both to run a reboiler in the amine wash in the subsequent CO_2 removal and to pre-heat the feed.

The invention is illustrated further with reference to the figure, where the present invention is combined with Applicant's GECCO™ technology for digester and landfill gas conditioning. The feed gas is heated to 200-450°C and fed to a siloxane or silanol absorption bed comprising alumina, alumina with nickel, silica or combinations thereof. After siloxane removal, the gas is fed to a catalytic reactor containing a catalyst selected from tungsten, vanadium, molybdenum, platinum and palladium in metallic or metal oxide form supported on a TiO_2 carrier. In this catalytic reactor, the catalyst converts the sulfur compounds to SO_2 and the VOC compounds (not methane and light [i.e. C3 and lower] hydrocarbons) to CO_2 and water and also hydrogen halides if some of the VOCs are halogenated.

One or more components suitable for catalytic oxidation, i.e. H_2, CO, ammonia, urea, methanol, ethanol, DME etc., is/are injected into the main gas stream containing oxygen, and the gas stream is fed to the catalytic reactor containing a catalyst such as vanadium, tungsten, chromium, copper, manganese, molybdenum, platinum, palladium, rhodium or ruthenium in metallic or metal oxide form supported on a carrier selected from alumina, titania, silica and ceria or combinations thereof. In the reactor, the injected component(s) is/are selectively oxidized to H_2O and CO_2, while the valuable hydrocarbons, such as methane and light [i.e.

C3 and lower] hydrocarbons, are substantially not converted. It is preferred that the catalyst comprises tungsten, vanadium, molybdenum, platinum or palladium in metallic or metal oxide form supported on a TiO_2 carrier.

The hot reactor exit gas can be utilized to heat the reactor inlet gas by using a feed-effluent heat exchanger.

The additional heat generated in the oxygen removal step will provide a higher temperature difference for the feed-effluent heat exchanger, which reduces the CAPEX.

Downstream from the heat exchanger, the SO_2 is removed in a wet caustic or H_2O_2 scrubber or a dry scrubber using a caustic sorbent. After the SO_2 removal, CO_2 is removed by using amine-based technology, solvent-based CO_2 removal technology, water-based CO_2 removal technology or alternatively PSA and/or membrane technology.

Nitrogen removal can be accomplished using membrane or PSA based technology. Then water is removed by using cooling and condensation followed by a molecular sieve, alternatively in a TSA configuration. Alternatively, the nitrogen removal unit is positioned downstream from the water removal unit.

It is further preferred that the catalyst used for sulfur and/or oxygen removal is monolithic to decrease the power consumption for transport of the landfill gas through the cleaning section.

Claims:

1. A method for the removal of oxygen from an industrial gas feed containing VOCs, sulfur compounds and/or chlorine compounds and optionally siloxanes and silanols, said process comprising in sequence the steps of:

(a) heating the feed gas,

(b) optionally removing siloxanes and silanols from the heated feed gas,

(c) oxidizing in the heated feed gas any or all of the VOCs to CO2, oxidizing the sulfur-containing compounds to SO2 and/or oxidizing the chlorine-containing compounds to CO2 and HCl,

(d) removing SO2 and/or HCl in a wet caustic or H2O2 scrubber or in a dry scrubber using a caustic sorbent,

(e) injecting one or more reactants selected from H2, CO, ammonia, urea, methanol, ethanol and dimethyl-ether (DME) for oxygen conversion into the heated feed gas from step (d),

(f) carrying out a selective catalytic oxygen conversion in at least one suitable reactor, and

(g) cleaning the resulting oxygen-depleted gas.

2. Method according to claim 1, wherein the gas feed, from which oxygen is to be removed, is a landfill gas, a digester gas or an industrial CO_2 off-gas.

3. Method according to claim 1 or 2, wherein the cleaning in step (g) comprises removal of CO_2 in a separation unit, removal of N_2 and drying of the cleaned gas.

4. Method according to any of the claims 1-3, wherein the gas has a high content of nitrogen and oxygen, and wherein two reactors with cooling in between are used for the selective catalytic oxygen conversion in step (f).

5. Method according to claim 4, wherein the heat recovered after each reactor is used in a re-boiler in the CO_2 separation unit.

6. Method according to claim 1 or 2, wherein the feed gas is heated to a temperature of between 150 and 450°C.

7. Method according to claim 1 or 2, wherein the feed gas is heated to a temperature of between 150 and 450°C and thereafter fed into step (b) and/or step (c).

8. Method according to claim 7, wherein the feed gas is heated through heat exchange with the effluent gas from the oxygen removal step prior to be fed into step (b) and/or step (c).

9. Method according to claim 2, wherein the landfill gas contains H_2S and organic sulfur compounds, CO_2, H_2O, methane, VOCs and optionally siloxanes and silanols.

10. Method according to any of the preceding claims, wherein the catalyst for the oxygen conversion comprises a metal selected among vanadium, tungsten, chromium, copper, manganese, molybdenum, platinum, palladium, rhodium and ruthenium in metallic or metal oxide form supported on a carrier selected from alumina, titania, silica and ceria.

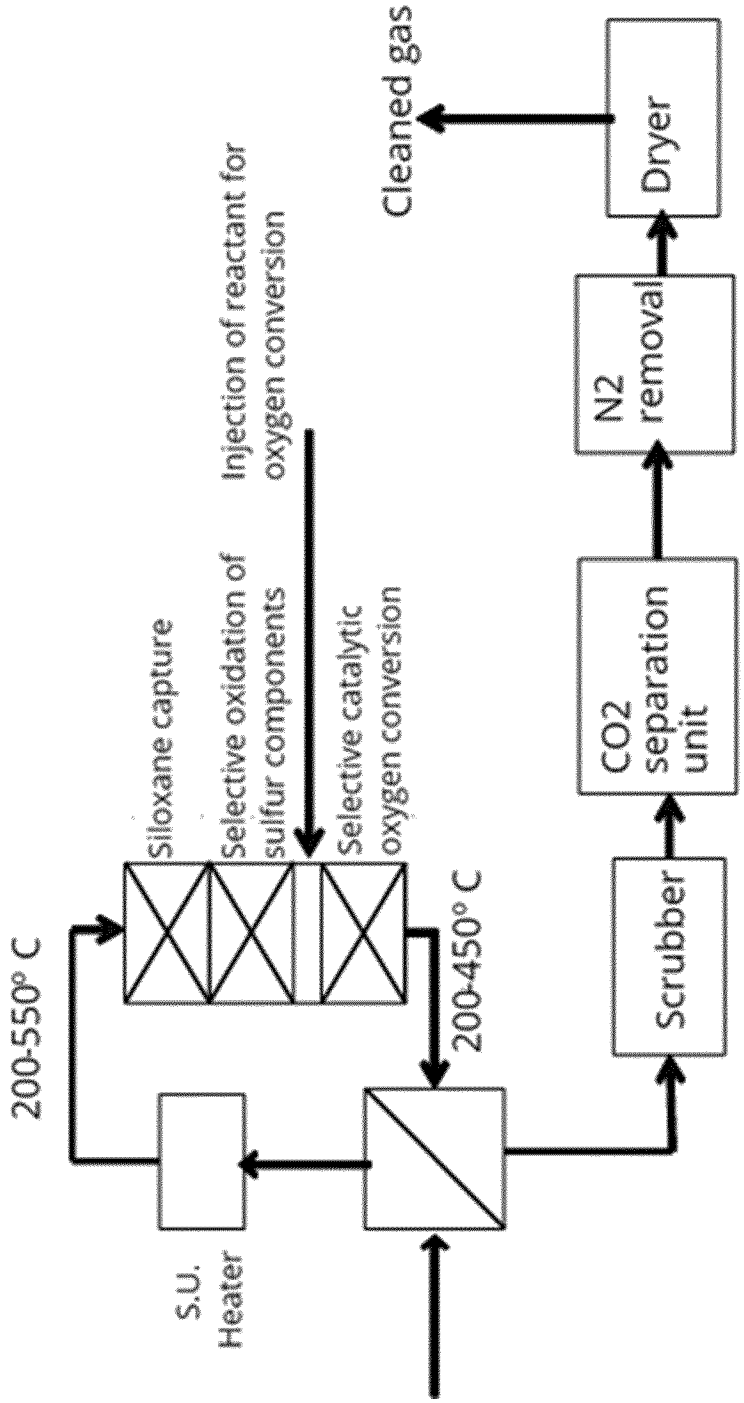
Cleaned gas
Dryer
N2 removal
CO2 separation unit
Scrubber
Injection of reactant for oxygen conversion
Siloxane capture
Selective oxidation of sulfur components
Selective catalytic oxygen conversion
200-550° C
200-450° C
S.U. Heater

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/053027

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/50 B01D53/86
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	URBAN W ET AL: "Catalytically upgraded landfill gas as a cost-effective alternative for fuel cells", JOURNAL OF POWER SOURCES, ELSEVIER SA, CH, vol. 193, no. 1, 24 December 2008 (2008-12-24), pages 359-366, XP026150425, ISSN: 0378-7753, DOI: 10.1016/J.JPOWSOUR.2008.12.029 [retrieved on 2009-06-03] Section "The process consists of three main stages"; page 361, right-hand column page 362; figure 2 Last paragraph of "Introduction"; page 360, right-hand column ----- -/--	1-10

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/053027

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 466 554 A (JOHNSON MATTHEY PLC [GB]) 30 June 2010 (2010-06-30) page 1, line 2 - line 12 page 4, line 25 - line 29 page 4, line 32 - page 5, line 3 page 9, line 36 - line 37 page 12, line 23 - line 24 -----	1-10
Y	WO 2012/006729 A1 (QUADROGEN POWER SYSTEMS INC [CA]; PRASAD ALAKH [CA]; MARCHAND KEVIN [C) 19 January 2012 (2012-01-19) paragraphs [0001], [0002], [0017] figure 1 -----	1-10
Y	JP 2011 153245 A (SUMITOMO SEIKA CHEMICALS) 11 August 2011 (2011-08-11) Paragraph "Subject of Invention" figure 1 claims 1, 2, 5 paragraph [0017] -----	1-10

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2018/053027

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