Abstract: Siloxanes and sulfur containing compounds from biogas streams from landfills and anaerobic digesters are removed in one process comprising the steps of heating the biogas and feeding it to an absorber containing a siloxane absorption bed, feeding the siloxane-free gas effluent from the absorber to a converter containing a sulfur monolith catalyst, where organic and inorganic sulfur compounds are oxidized to sulfur dioxide, cooling the hot exit gas from the converter and removing sulfur dioxide from the cooled gas. This way, a purified gas stream free of siloxanes and sulfur compounds is obtained.
Title: A process and a gas treatment system for combined removal of siloxanes and sulfur containing compounds from biogas streams

The present invention relates to a process for the combined removal of siloxanes and sulfur containing compounds from biogas streams, more specifically biogas streams from landfills and anaerobic digesters. The invention further relates to a gas treatment system for carrying out the process.

Biogas is typically a waste product from sources including landfills and anaerobic digesters. In general, biogas contains approximately 50-75% methane, 25-50% carbon dioxide, 0-10% nitrogen, 0-1% hydrogen, 0.1-3% sulfur and 0-2% oxygen, all by volume. It also contains an assortment of impurities that can include siloxanes as well as chlorine, volatile organic compounds (VOCs) and ammonia. Because biogas is typically generated from organic matter, it is generally considered a renewable form of energy.

Since biogas contains methane, it is convertible to a biogas fuel for power or heat generation. However, it needs to be cleaned first. One of the reasons that biogas should be cleaned prior to use is that sulfur impurities in biogas can create a corrosive environment inside power generating equipment or even poison catalysts that may be present. Furthermore, 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. Another reason to clean biogas 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 biogas 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.

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. 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 SiO2 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 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\textsubscript{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\textsubscript{2} tolerance can be as low as 250 ppb.

For the reasons outlined above it is desirable to remove siloxanes and sulfur containing compounds from gas streams to increase the engine service time and the catalyst lifetime.

According to the present technology in the field, separate units are used to carry out the removal of siloxanes and the removal of sulfur containing compounds. Thus, in WO 2006/104801 A2 a siloxane removal process is described, where biogas released from landfills and sewage treatment plants is freed of siloxane contaminants by passing biogas at a temperature of 35-50°C through a bed containing activated alumina, which adsorbs the siloxanes. When the activated alumina becomes saturated with siloxanes, the adsorption capability of the activated alumina is recovered by passing a regeneration gas through the bed of activated alumina. In a system with two or more beds of activated alumina, one bed is used to remove siloxanes, while one or more of the other beds are being regenerated.

WO 2008/024329 A1 discloses a system comprising an adsorbent bed for removing siloxanes from biogas down to a very
low siloxane level, so that the cleaned biogas can be used as intake air for equipment, such as combustion engines or gas turbines. The sole specific example in the description indicates a reaction temperature in the adsorption towers of between -28.9°C and 121°C. The adsorbent bed comprises at least two of activated carbon, silica gel and a molecular sieve.

In US 9,039,807 B2, another regenerative adsorption process for siloxane removal is described. This process uses an adsorbent having a neutral surface, and it is used at a temperature of around 35-50°C. When the adsorbent bed is filled to capacity, it is heated to remove the siloxanes and regenerate the bed.

Regenerable systems using activated alumina, activated alumina plus silica and activated carbon adsorbents to capture the siloxanes have been reported. After saturation of the adsorbent with siloxane impurities, the adsorbed siloxanes are removed in situ using pressure swing adsorption (PSA) or thermal swing adsorption (TSA) to enable the bed to be re-used. An example of a TSA unit for siloxane removal is disclosed in the aforementionedWO 2006/104801 A2.

Siloxanes can be removed from naphtha streams by using an adsorption process that requires a high temperature (300-350°C) to be reasonably efficient. Thus, high temperature adsorption is known to be effective in areas (e.g. treatment of naphtha streams) where high temperatures are typical, but it is unfeasible in itself when treating low temperature gas streams because of the energy costs involved in heating up and subsequently cooling down the gas.
Regarding the removal of sulfur containing compounds, such as \( \text{\delta S} \), from biogas streams, this can be done by adsorption on e.g. activated carbon at temperatures of 50-70°C. Iron oxides like FeO can also be used as adsorbents, typically as so-called iron sponge (wood chips impregnated with iron oxides) at temperatures of 25-50°C.

Processes and products exist for oxidation of \( \text{\delta S} \) and other inorganic sulfur compounds such as COS and \( \text{CS}_2 \) as well as organic sulfur compounds such as thiols and mercaptans. Thus, EP 2 878 358 A1, belonging to the applicant, describes a process for catalytic oxidation of a gas comprising \( \text{\delta S} \) and also one or more of CO, COS and \( \text{CS}_2 \) by contacting the gas with two consecutive catalytically active materials, the first of which being active in oxidizing \( \text{\delta S} \) at a given first temperature and the second being active in oxidizing CO, COS and/or \( \text{CS}_2 \) at a second, higher temperature.

Specific catalysts for the oxidation of sulfur compounds are disclosed in EP 2 878 367 A1, also belonging to the applicant. These catalysts, commonly called sulfur monolith catalysts (SMCs), are active in the oxidation of \( \text{\delta S} \) at temperatures as low as 200°C, and they are most effectively operated using a 250-350°C hot inlet gas stream. Typical SMC designs will therefore include a feed/effluent heat exchanger to heat up the inlet gas stream before entering the SMC reactor.
The major problem concerned with the above technologies to remove siloxanes and sulfur containing compounds from biogas streams, especially biogas streams from landfills and anaerobic digesters, is that they add up to significant capital costs as well as operational costs. They also add significantly to the operation and equipment complexity for these relatively small treatment units. Further, as mentioned above, known effective siloxane removal technologies from other fields, such as naphtha, require high temperatures. It would therefore be desirable to find an economically feasible combination method for the removal of both siloxanes and sulfur containing compounds from biogas streams.

WO 2012/006729 A1 describes an integrated cleaning system to remove water, siloxanes, sulfur, oxygen, chlorine and volatile organic compounds (VOCs) from biogas originating from landfills and digesters, thereby obtaining clean biogas for heat and power generating systems such as boilers, engines, turbines or fuel cells. Siloxanes, chlorine, oxygen and sulfur are removed to ppb levels. 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 hydro-desulfurization bed and adsorbent media beds. Heat exchange arrangements provide efficient recycling of waste heat and compensation for varying levels of oxygen in the incoming biogas waste stream, suitable for use in a wide range of biogas generating sources. The resulting biogas fuel product is suitable for use in combustion generators, fuel cell
systems, greenhouse boilers, or as feedstock for further upgrading to renewable natural gas.

While the system of WO 2012/006729 A1 is able to handle a number of contaminant problems in biogas, it is obviously a complicated and demanding system which is very expensive to establish. For this reason, it is not suited for specific removal of only siloxanes and sulfur containing compounds, the two most problematic contaminants in biogas streams.

It has now surprisingly turned out that a combination of the (efficient high temperature) siloxane removal technology with the SMC catalyst technology for oxidation of $\frac{1}{4}S$ and other inorganic sulfur compounds, such as COS and CS$_2$, as well as organic sulfur compounds, such as thiols and mercaptans, leads to desirable cleaning results obtained under conditions that do not add up to significant capital costs or operational costs.

More specifically, the present invention relates to a process for the combined removal of siloxanes and sulfur containing compounds from biogas streams, more specifically biogas streams from landfills and anaerobic digesters, said process comprising the steps of

- heating the biogas and feeding it to an absorber, which contains a siloxane absorption bed,

- feeding the siloxane-free gas effluent from the absorber to a converter containing a sulfur monolith catalyst, where organic and inorganic sulfur compounds are oxidized to sulfur dioxide,
- cooling the hot exit gas from the converter and
- removing sulfur dioxide from the cooled gas,

whereby a purified gas stream free of siloxanes and sulfur compounds is obtained.

US 2015/0119623 A1 describes a method of removing siloxanes and sulfur containing compounds from a biogas. The siloxane compounds are removed by converting them to S1O₂ over a catalyst comprising Al₂O₃ maintained at a temperature of at least 200°C. The S1O₂ is embedded in the pores of the Al₂O₃. The sulfur containing compounds are removed by catalytic oxidation over a V₂O₅ catalyst, whereby SO₂ is formed, followed by passing the SO₂ containing biogas over a sorbent, such as alkaline impregnated carbon. The purified biogas is combusted and the hot exhaust gases are used to heat the purification steps.

The subject matter of the present invention differs from that of US 2015/0119623 A1 in that the siloxanes are removed by absorption and that the biogas is cooled prior to removing SO₂.

Preferably a feed/effluent heat exchanger is used to heat the raw feed gas and simultaneously cool the exit gas from the converter. In this embodiment, the heat generated in the catalytic reaction is specifically used to heat up the gas to the siloxane absorber with the purpose of increasing its operating temperature and improve its performance.
The invention also relates to a gas treatment system for carrying out the above process. Said system comprises an absorber containing a siloxane absorption bed and a converter containing a catalyst for the oxidation of sulfur compounds and volatile organic compounds present in the gas, the absorber and the converter being connected so that the siloxane-free gas effluent from the absorber is fed to the inlet of the converter.

Preferably the system also comprises a feed/effluent heat exchanger to heat the raw feed gas and simultaneously cool the exit gas from the converter. The system further comprises a unit for removing sulfur dioxide from the cooled exit gas from the converter, said unit preferably being a scrubber.

The appended figure shows a preferred embodiment of the process and the gas treating system according to the invention. In this embodiment, a siloxane absorption bed (Abs.) is installed between a feed/effluent heat exchanger (HEX) and the converter (Conv.), which contains a sulfur monolith catalyst. This preferred embodiment further includes a scrubber (Scrub.) used for removing sulfur dioxide from the cooled exit gas from the converter. Quench water is pumped to the scrubber together with a caustic substance, such as NaOH, to remove SO₂. The waste water is drained off in the scrubber, leaving a purified product gas.

In this reactor configuration, the cool raw gas coming from a landfill or an anaerobic digester will first be pumped through the feed/effluent heat exchanger, in which it will be heated to a temperature around 300–350°C. Then the hot
gas will pass through the siloxane removal bed, where the siloxanes present in the gas will be absorbed. The siloxane-free gas will then enter the SMC converter, where organic and inorganic sulfur containing compounds are oxidized to sulfur dioxide. The SMC will also facilitate oxidation of VOCs to their corresponding combustion products, however not to methane and, most likely, also not to lower alkanes up to C3. The oxidation reactions are exothermic, and the SMC is typically designed to a maximum outlet temperature of about 450°C.

The hot exit gas is then passed through the feed/effluent heat exchanger, where it is somewhat cooled down. This cooled gas is subsequently subjected to sulfur dioxide removal, preferably in a scrubber as described above.
Claims:

1. A process for the combined removal of siloxanes and sulfur containing compounds from biogas streams from landfills and anaerobic digesters, comprising the steps of

- heating the biogas and feeding it to an absorber, which contains a siloxane absorption bed,

- feeding the siloxane-free gas effluent from the absorber to a converter containing a sulfur monolith catalyst, where organic and inorganic sulfur compounds are oxidized to sulfur dioxide,

- cooling the hot exit gas from the converter and

- removing sulfur dioxide from the cooled gas,

whereby a purified gas stream free of siloxanes and sulfur compounds is obtained.

2. Process according to claim 1, wherein a feed/effluent heat exchanger is used to heat the raw feed gas and simultaneously cool the exit gas from the converter.

3. A gas treatment system for carrying out the process according to claim 1 or 2, said system comprising an absorber containing a siloxane absorption bed and a converter containing a catalyst for the oxidation of sulfur compounds and volatile organic compounds present in the gas, the ab-
sorber and the converter being connected so that the silox-
ane-free gas effluent from the absorber is fed to the inlet
of the converter.

4. Gas treatment system according to claim 3, said
system also comprising a feed/effluent heat exchanger to
heat the raw feed gas and simultaneously cool the exit gas
from the converter.

5. Gas treatment system according to claim 3, said
system further comprising a unit for removing sulfur diox-
ide from the cooled exit gas from the converter, said unit
preferably being a scrubber.
A CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/14 C10L3/10
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 CIOL

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

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<td>US 2015/119623 AI (HUANG FRANCIS Y [US]) 30 April 2015 (2015-04-30) cited in the application figure 1 paragraphs [0001], [0010], [0027], [0033], [0047], [0048], [0052], [0053], [0062] -----</td>
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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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Date of the actual completion of the international search: 28 April 2017

Date of mailing of the international search report: 11/05/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Burkhardt, Thorsten
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<td>WO 2013/128001 AI (BASF SE [DE]; RES TRIANGLE INST [US]) 6 September 2013 (2013-09-06) page 5, line 37 - page 6, line 5 page 8, line 37 - line 38</td>
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