



Removal of sulfur contaminants from biogas to enable direct catalytic methanation

Christian Dannesboe¹ · John Bøgild Hansen² · Ib Johannsen¹

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Abstract

In the near future, renewable energy sources will replace fossil energy. To allow full carbon utilization of renewable biomass, we have demonstrated a possible integration between a biogas reactor, an electrolysis unit, and a catalytic methanation reactor. Stringent removal of all sulfur contaminants in raw biogas is required to enable this integration. We demonstrate how existing bulk sulfur removal solutions, like a biotrickling filter loaded with *Acidithiobacillus thiooxidans* and impregnated activated carbon, are unable to meet this requirement. Only the main sulfur contaminant hydrogen sulfide (H₂S) can effectively be removed. Contaminants carbon disulfide (CS₂), dimethyl sulfide (DMS), and carbonyl sulfide (COS) will leak through the carbon filter, long before hydrogen sulfide can be detected. Utilization of surplus oxygen from the combined system is proven problem free and allows sulfur removal without introducing contaminants. Provided that a recommended sulfur guard is included, the proposed design is ready for full-scale implementation.

Keywords Biotrickling filter · Carbon filter · Biogas methanation · Biogas contaminants · Power to methane

1 Introduction

Production of energy from biomass is one of the technologies enabling a fossil-free future. In Northern Europe, biogas facilities are widespread [1], and many of the plants built just 10 years ago are extending their processing capability [2].

Highlights

- Pure oxygen available from the electrolysis of the combined power-to-methane system removes nitrogen contamination.
- H₂S is efficiently removed using impregnated activated carbon; however DMS and CS₂ leak through.
- The proposed treatment removes biogas contaminants to a level enabling direct methanation.

✉ Christian Dannesboe
chda@eng.au.dk

John Bøgild Hansen
jbh@topsoe.com

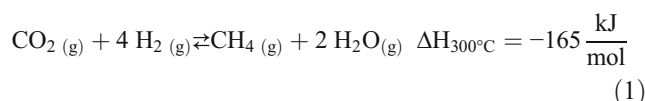
Ib Johannsen
ibj@eng.au.dk

¹ Department of Engineering, Aarhus University, Hangeovej 2, DK-8200 Aarhus N, Denmark

² Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kongens Lyngby, Denmark

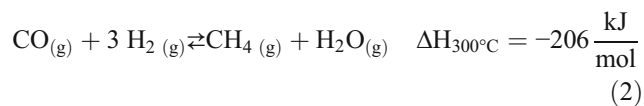
Production of biogas is used as an efficient way to handle waste streams from agricultural production facilities, and biogas reactors at wastewater treatment plants are being installed to reduce the overall energy requirement. The produced biogas is carbon neutral, and the main component in the biogas, methane (~55–70%), is easily moved from producer to consumer/storage via the existing natural gas grid. Export of methane to the grid will require the main byproduct in biogas, CO₂ (~30–45%), to be removed on-site [3]. Several proven separation systems are available like amine or water scrubbers as well as pressure swing adsorption. The success of biogas is not without limitations. Available biomass is a restricted resource, and replacing natural gas in this way will not be possible. Currently gas consumption is at a high level in multiple sectors: industrial, district heating, and transport [4].

A way to provide a substantial boost to biogas plant methane output is to include a methanation reactor in the plant design, enabling conversion of the by-product CO₂ to more methane via the Sabatier reaction [5] (Eq. 1).



Catalytic methanation of carbon monoxide (CO) is often considered along with the Sabatier reaction, and this reaction

will release even more energy (Eq. 2). The content of CO in biogas is however very low and primarily found in gas from landfills [6].



Catalytic methanation technology has been proven for decades on syngas from various sources [7]. This enables production of synthetic natural gas using H₂ and a mixture of CO and CO₂. Using a biogas feed without CO for the catalytic methanation results in a reduced adiabatic temperature and reduces the risk of carbon formation in the reactor [8, 9]. From a safety perspective, it is also easier to manage plant maintenance activities when the very toxic CO is not present. The mechanism of catalytic CO₂ methanation is still being discussed [10], as results from different groups point towards two different pathways. Results from Eckle et al., Karelovic and Ruiz, as well as Akamaru et al. point towards a CO intermediate based on catalyst containing Ru or Rh [11–13]. However, the findings of Aldana et al., Pan et al., as well as Park and McFarland [14–16] indicate CO₂ adsorption to the catalyst support and subsequent hydrogenation to methane. These last studies are done with Ni or Pd catalyst and propose formate or carbonate as the intermediate but also highlight the importance of the support material. Methanation plants operating on pure CO₂ sources have been in operation for years [17], whereas direct CO₂ methanation in biogas is a rather new idea with pilot plant activities booming since 2013 [18].

Continued development of electrolyzer technologies, like alkaline, proton exchange membrane, and solid oxide electrolysis cells (SOEC), has enabled a cheap and fossil-free hydrogen production from photovoltaics and wind farms [19]. Specifically SOEC-based electrolyzers are able to utilize several synergies when combined into electrolyzer–methanation units, enabling methanation of CO₂ directly in biogas [20]. The first results from such combined pilot facilities are now becoming available (2019), showing potential for a very high plant efficiency [9, 21]. Full integration between biogas production, electrolysis, and catalytic methanation will boost the methane output by 40–80% and ensure full utilization of carbon from biomass. The individual technologies are already available at an industrial scale, indicating that a single, cheap, full-scale solution for direct upgrading of biogas is soon to become available.

The focus of this paper is the challenge of deep sulfur removal at biogas sites using proven sulfur treatment solutions like a biotrickling filter and/or impregnated activated carbon. Deep sulfur removal will be required to enable direct catalytic methanation of biogas, as sulfur contamination, even in the range of 1–10 ppb_v, is known to cause problems [22]. The

potential benefits of utilizing the surplus oxygen stream from the integrated electrolyzer–methanation unit are evaluated.

1.1 Technical aspects of biogas treatment

The main concerns with regard to export of methane from biogas facilities are high levels of CO₂ and hydrogen sulfide (H₂S) as well as a high moisture level [1, 2, 23, 24]. A simple gas dryer easily reduces the specified requirements on dew point to acceptable levels, but CO₂ and H₂S are more complicated to remove.

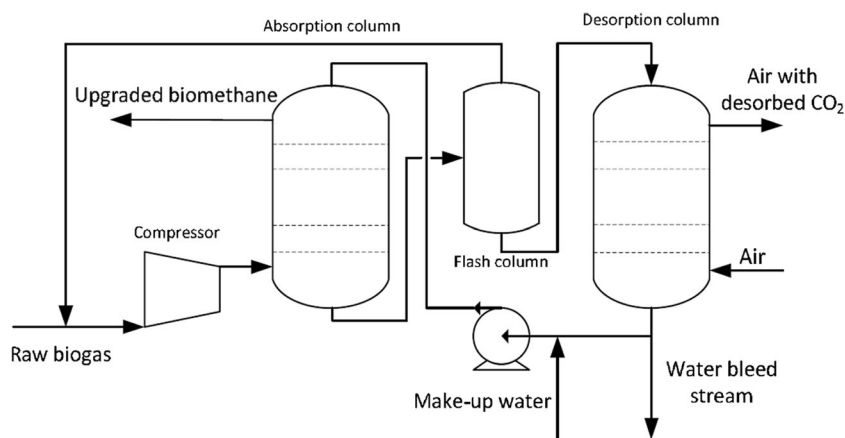
1.1.1 Removal of CO₂

The removal of CO₂ can be performed by several technologies like membranes, pressure swing adsorption (PSA), or chemical scrubbers. Chemical scrubbers use solvents like methyldiethanolamine (MDEA), polyethylene glycol mixtures, or water. According to Sheets and Shah [25], this last type of CO₂-scrubber using pressurized water is the most common biogas cleaning method (used at ~40% of all projects worldwide). Comparison of different CO₂ removal technologies as well as current operational costs can be found in the review by Bauer et al. [1]. This review covers CO₂ removal technologies used in Northern Europe (Sweden, Germany, the Netherlands, UK, and Denmark). Even the earliest commercial technologies like pressurized water scrubbing (Fig. 1) and PSA have a low methane slip and will recover more than 97% of the methane [1].

Updated designs are showing further improvements, and a new technology like the MDEA scrubber is delivered with a guarantee of 99.9% methane recovery [26]. In newer unit designs, H₂S is always removed before the CO₂ separation step to reduce risk of corrosion and to ensure subsequent release of CO₂ to the atmosphere does not cause health or smell concerns. Although a stream rich in CO₂ is made available by the removal process, recovery and reuse are yet to become the norm. The CO₂ is typically diluted with strip air and contains the contaminants CH₄, H₂O, as well as trace amounts of H₂S. Because of this, it has limited value and use. Strip air is not introduced in membrane units nor in the MDEA scrubber [1]. These technologies are likely to be the first to find use of CO₂ as a resource. An important note on all CO₂ removal technologies is the term “upgrading,” often used to describe the removal process. With CO₂ removal, it becomes possible to inject the remaining methane to a national gas grid, but in all cases, the CO₂-carbon from biomass is wasted, making the name misleading.

As biogas consists primarily of CH₄ and CO₂ in almost equal amounts, the removal of CO₂ will almost double the concentration of contaminants like nitrogen (N₂) or oxygen (O₂), as these cannot be effectively removed by any of the technologies.

Fig. 1 Sketch of a pressurized water scrubbing unit for CO₂ removal. From Bauer et al. [1]

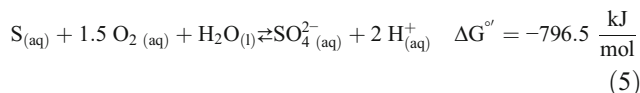
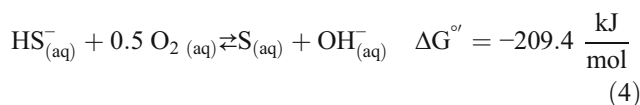
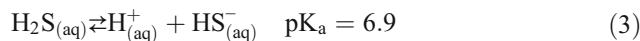


1.1.2 Removal of H₂S

As H₂S is corrosive, it is preferably the contaminant removed first. A common large-scale removal option is biological oxidation in a biotrickling filter (BTF), using conditions favoring conversion by *Acidithiobacillus thiooxidans* [24, 27]. This technique involves oxidation of hydrogen sulfide (H₂S_(g)) to sulfur (S_(s)) or an even higher oxidation state of sulfur (e.g., sulfuric acid, H₂SO₄). The BTF is robust and requires low maintenance, providing a cheap removal of bulk hydrogen sulfide (from ~1500 ppm_v to ~30 ppm_v levels) [24, 28, 29]. The process of micro-aeration directly in the digester head-space results in the same biological processes. This can be performed if corrosion is not an issue. Typically, this would require a secondary digester. Micro-aeration is a common way to reduce high sulfur levels (from > 3000 ppm_v to ~800 ppm_v levels) [30]. In case further reduction of the hydrogen sulfide level is required, the biological treatment can be combined with a downstream polish using activated carbon (from ~500 ppm_v to ~1 ppm_v levels) (Fig. 2) [1, 2, 23, 31]. All technologies typically inject air as the O₂ source when operating at industrial scale [24, 29]. At sites treating high levels of H₂S (> 10,000 ppm_v), the resulting nitrogen contamination may become a restriction, and the added cost of pure oxygen injection has to be accepted [29, 30, 32].

The biochemical mechanisms used by *A. thiooxidans* when oxidizing reduced sulfur components are still being identified [33], but results indicate several pathways that may run independent of each other. Oxidizing H₂S to sulfur will provide energy (Eq. 4), but if a pathway from sulfur to sulfuric acid is appended, clearly more energy is made available to

A. thiooxidans (Eq. 5) [33–35]. The production of sulfuric acid results in a low pH of 1–2, and this environment is intolerable to most other organisms [29].



After the bulk removal in the BTF, the remaining H₂S can be removed by adsorption to activated carbon. The technology is fully proven; active carbon is cheap and has a high capacity [36–38]. At some biogas facilities, activated carbon may be the only removal technique installed to reduce investment cost and minimize air contamination [2]. Active carbon has a limited physical adsorption capacity of H₂S (Eq. 6), whereas the chemical adsorption of elemental sulfur is very high [37]. Impregnating the carbon with alkali ensures chemical absorption is favored. H₂S adsorbs to the carbon where it is oxidized to sulfur (Eq. 7) [37]. Adding a promoter like potassium iodide acts as an oxidation catalyst and at the same time reduces formation of unwanted sulfuric acid [36].

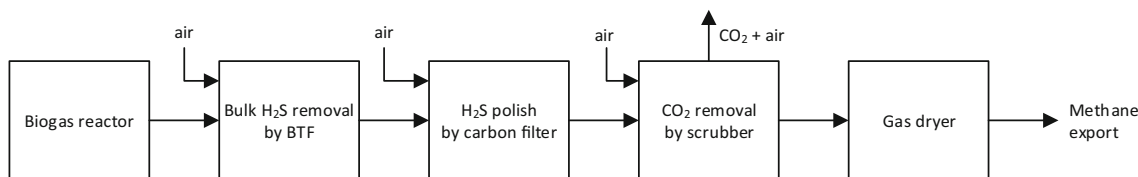
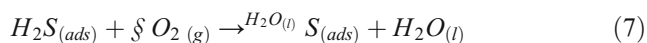


Fig. 2 Typical treatment of biogas before methane export



The oxidation reaction occurs in a water film at the surface of the carbon particle. Both the biogas reactor and the BTF will saturate the biogas with water, ensuring the moisture requirement by the impregnated carbon filter is always present (typically > 10% RH is required [39]). For this reason, a gas dryer should not be installed before a carbon filter when the purpose is H₂S removal [38].

Both the biological process and the impregnated activated carbon will require O₂ (Eqs. 4, 5, and 7) for the sulfur oxidation reaction [33, 35, 37]. The cheapest O₂ source is air, and injecting air both in the BTF and carbon filter is a common practice [24, 38]. As a result of H₂S removal by the BTF and carbon filter, new contaminants, N₂ and O₂, are introduced [23, 30, 40]. As N₂ is nonflammable, it is undesired in the final methane, and air injection is normally kept at a minimum. Addition of O₂ at only the stoichiometric requirement would in principle ensure complete conversion of O₂ and minimal N₂ contamination, but in all practical applications, a surplus of O₂ is required to ensure sufficient driving force and to avoid equilibrium restrictions [28–30]. Providing O₂-enriched air or pure O₂ will indeed improve the conversion of H₂S, but due to the cost of pure O₂, this addition is only done at sites where the nitrogen contamination cannot be accepted [29, 30, 32]. One recent cost study finds the use of highly enriched air as the most cost-effective solution when the initial sulfur level is 2300 ppm_w [32]. In case of O₂ contamination from the H₂S cleaning step, this remains a significant issue as potential incorrect dosing of air/oxygen provides a safety concern. Residual oxygen also restricts export options. Different acceptable levels of residual oxygen are the only reason natural gas from Denmark cannot be exported to Germany. The presence of H₂ and O₂ in the downstream catalytic methanation reactor will effectively produce water. This removes all concerns of residual oxygen in the final gas.

1.1.3 Requirements for the catalytic methanation reactor

The performance of a fixed bed methanation reactor loaded with a nickel catalyst (Ni/Al₂O₃) has been proven as a reliable technology for pure CO₂ methanation [8, 10, 17, 41, 42]. When upgrading CO₂ directly in biogas, the main differences in the reactor design are [9, 21, 43–45]:

- Heat management of the highly exothermic reaction is easier as the high methane content acts as a heat sink.
- The methane already present in biogas will affect the equilibrium reaction and restrict the conversion of CO₂.

The methanation catalyst is very sensitive to sulfur poisoning. Extensive analysis in the chemisorption of sulfur on Ni/Al₃O₂ and similar catalysts has made this one of the most

studied catalyst poisonings [22]. Multiple older references recommend a sulfur level in the range of 100 ppb_v for efficient operation of methanation catalyst [46–48]. Newer guidelines note significant catalyst site coverage at levels as low as 1–10 ppb_v [22]. Detecting sulfur at this level represents a significant analytical challenge only recently available to researchers [49]. Since chemisorption of sulfur is a reversible process, several guidelines on catalyst regeneration are available [50, 51]. The chemisorption process is exothermic and is well described by a Temkin isotherm [52]. A nickel catalyst fully deactivated by 100 ppm_v H₂S at 700 °C was shown to “only” deactivate by 70% at 800 °C still in the presence of 100 ppm_v H₂S. This temperature however promotes catalyst damage by sintering [10]. Operating the CO₂ methanation reactor at a temperature around 300 °C, as recommended in earlier work [9], would essentially make the chemisorption of H₂S irreversible [22]. An alternative catalyst regeneration method is steam oxidation at around 650 °C. This has been demonstrated as an effective way to remove chemisorbed H₂S from nickel [50, 51]. Although H₂S is the dominant sulfur compound in biogas, several other sulfur compounds like COS, DMS, CS₂, and thiophene also contribute to sulfur poisoning of Ni/Al₃O₂ catalysts [53–56]. The study by Czekaj et al. [54] finds COS to bind strongly to the catalyst support rather than nickel. As the catalyst is reactivated, the COS is not as effectively removed. Results suggest COS is responsible for re-poisoning of nickel when methanation is resumed. As such, it is crucial to remove all sulfur species in the feed gas, not just H₂S. A very effective sulfur adsorbent will be required to reach ppb_v levels of all sulfur contaminants. Current biogas treatment solutions using activated carbon as the final step reduce the H₂S level down to 1–2 ppm_v [23]. Frequent replacement could make this solution reach a lower H₂S level, but organic sulfur species cannot be expected to be effectively removed [38]. Deep sulfur removal at biogas sites is a proven challenge [57], and no general guidelines are currently available [38].

1.2 Aim of this study

Future power-to-methane systems will rely on direct catalytic methanation of biogas. With a pure O₂ stream available from the on-site electrolyzer, it is possible to replace air injection to the BTF and carbon filter, thereby eliminating the N₂ contamination. The proposed integration is shown in Fig. 3.

The performance of these technologies when operated on pure oxygen was investigated. A study on the deep sulfur removal limitations of impregnated activated carbon was evaluated as well. The following studies were performed:

- The minimum oxygen requirement was determined for a bench-scale biotrickling filter operated on raw biogas. The

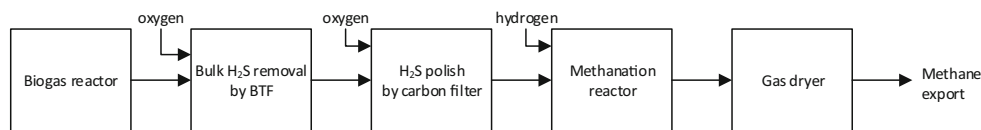


Fig. 3 Proposed integrated treatment of biogas before methanation and export. Hydrogen and oxygen are provided by electrolysis

biotrickling filter was tested both with air injection and pure oxygen injection.

- Removal of sulfur contaminants was tested using a carbon filter operated on raw biogas. The filter was tested both with air injection and pure oxygen injection.
- Biogas treated by the carbon filter was analyzed with regard to hydrogen sulfide and other sulfur compounds at ppb_V levels.
- Biogas treated by the carbon filter was analyzed with regard to nitrogen and oxygen in the ppm_V range.

The results from these tests provide the much needed hard data to clarify on the potential benefits of pure oxygen injection as well as the need for a pre-reactor/sulfur guard in the final design.

2 Material and methods

In the following experiments, raw biogas was provided from the main biogas reactor at Aarhus University Foulum. Thermophilic digestion was performed with a temperature set point of 51 °C. Average retention time was 15 days. The biomass consisted of cow manure (approx. 60 t/d) mixed with plant-based materials (approx. 20 t/d) to achieve 14% dry matter in the feed. Plant-based material was a mixture of livestock bedding, extruded straw, meadow hay, and silage. The total gas production from the main reactor was approx. 150 Nm^3/d . The biogas was provided raw, i.e., before downstream sulfur removal using a biotrickling filter and before drying.

2.1 Bench-scale biotrickling filter

Basic system parameters of the bench-scale BTF were obtained from the full-scale BTF. This provided a ratio $H/D = 3$ of the filter medium and a reactor residence time of 1 minute. The bench-scale BTF was constructed from PVC pipe (plastic fittings, silicone tubing, no metal parts). The pipe had a diameter of 11 cm, a height of 116 cm, and allowed treatment of 165 NL/h biogas. A gas dispersion layer of lightweight expanded clay aggregate (Leca® Ø 10–20 mm) was placed before the filter medium (Fig. 4). The filter medium consisted of Leca with immobilized *A. thiooxidans*. The filter medium was kindly donated from a full-scale BTF in operation at Madsen Bioenergi I/S, Spøttrup, Denmark, ensuring a healthy biofilm had already been established (pH 1.5). The filter medium was

kept wet by purging water and nutrients (Rabasol Chemie, NPK 886, diluted 1:100) at a flow of 30 mL/h. The reactor was wrapped with a heating mat and kept at 28 °C. Small pumps delivered the flow of biogas and air. A constant gas flow was verified daily by flowmeter (Flonidan, SciFlo G4-6SOT). The O_2 and H_2S levels in the biogas were measured two times a day using a portable analyzer (Messtechnik EHEIM GmbH, VISIT 03). The H_2S content was in the range of 800–1200 ppm_V in the period of testing (2 months). Oxygen was provided in cylinders by Air Liquide (O_2 , 99.995%). The BTFs were operated for 3 days with no changes. After this stabilizing period, changes with air injection and injection of pure O_2 were made every second day (Mon, Wed, Fri). Oxygen injection was varied in the range 0.5–5%. Conversion of H_2S was calculated from a simple input/output comparison.

2.2 Carbon filter

Removal of H_2S and other sulfur compounds to ppb_V level was accomplished by impregnated alkaline activated carbon. The carbon filter was designed by Haldor Topsøe A/S, Kgs. Lyngby, Denmark, and constructed by Zeton B.V., Enschede, the Netherlands. The filter has an inner diameter of 26.5 cm and a height of 1.8 m. The filter has a carbon bed height of 1.4 m and allows treatment of 10 Nm^3/h biogas (Fig. 5). The filter is kept at 50 °C by electrical tracing. The impregnated

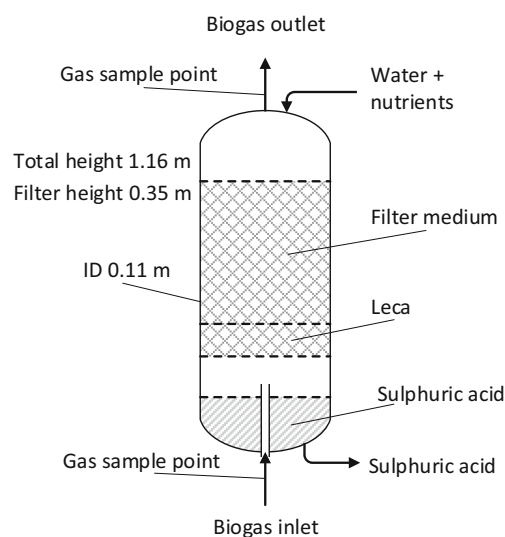


Fig. 4 Bench-scale biotrickling filter used for bulk H_2S removal. Treatment of 165 NL/h raw biogas. The filter was wrapped with a heating mat (not shown) at 28 °C

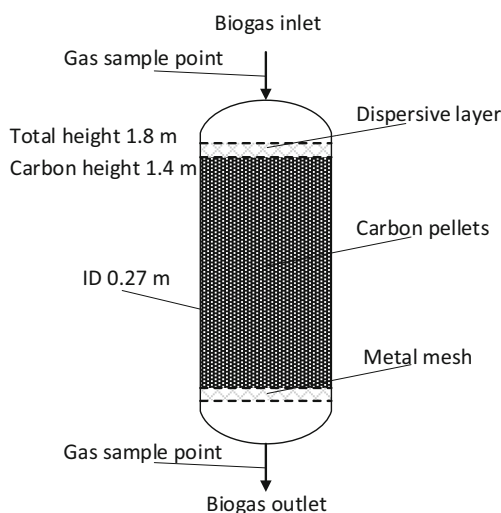


Fig. 5 Carbon filter used for the removal of H_2S . Treatment of $10 \text{ Nm}^3/\text{h}$ raw biogas. The filter was heated to $50 \text{ }^\circ\text{C}$ using electric tracing

alkaline activated carbon used was SOLCARB® KS3 from Chemviron Carbon, Lancashire, United Kingdom. Pellet diameter is 3 mm with a typical length of 7 mm [39]. This product is specifically designed for removal of sulfur compounds in biogas. For optimal removal of H_2S , an $\text{O}_2/\text{H}_2\text{S}$ stoichiometric ratio of 1.8 is recommended [39]. A CEM unit (Bronkhorst, W-202A) controls dosing of air or O_2 . The concentration of O_2 , N_2 , and H_2S in the biogas was measured in the ppm_V range using a dual channel (MS5Å and PPQ) GC equipped with a thermal conductivity detector. The GC setup and analysis were performed by accredited external lab (Dansk Gasteknisk Center, DGC), using their equipment on-site allowed online analysis. The H_2S content was in the range of $850\text{--}900 \text{ ppm}_\text{V}$ in the 4-hour period of the analysis. The filter had been processing 3500 Nm^3 of biogas at the time of the analysis. Assuming an average H_2S level of $1000 \text{ ppm}_\text{V}$, the carbon filter would have increased 9% in mass by sulfur adsorption at this point. Oxygen was provided in cylinders by AGA (O_2 , 99.995%). Through a valve setup, the GC was sampling from the filter inlet or outlet. Continued measurements were recorded over a period of approx. 1 hour for each test. Due to this setup, analysis of input and output could not be done simultaneously. The center ten data points of each interval was used in the statistical analysis. A paired Student's t test was performed with the software Minitab.

2.3 Analysis of H_2S and other sulfur compounds at ppb_V level

Analysis of H_2S and other sulfur compounds at ppb level was performed on triplicate samples taken after the carbon filter. The analysis was performed by GC analysis (Agilent Technologies, Gas Chromatograph System 7890A with dual plasma controller, 355 sulfur chemiluminescence detector,

J&W DB-1 60 m column ID 0.52 mm 5 μm film). The GC method is described in the publication by Liu [49]. To protect the detector from high concentrations of H_2S , the sample H_2S level was confirmed to be below 5 ppm_V H_2S by Kitagawa Tubes (Komyo Rikagaku Kogyo K.K., $0.75\text{--}37.5 \text{ ppm}_\text{V}$). The H_2S content was in the range of $800\text{--}1500 \text{ ppm}_\text{V}$ in the period of testing (45 days). Gas sample bags from Tedlar PVDF (SKC Ltd., Dorset, United Kingdom) were used to bring gas samples to the GC. The bags were analyzed within hours of sampling and were not reused. Samples were obtained straight after loading of carbon material to evaluate the performance of virgin activated carbon. The next set of samples was obtained after treatment of 4000 Nm^3 of biogas. The last set of samples were obtained after treatment of 8000 Nm^3 biogas. Assuming an average H_2S level of $1000 \text{ ppm}_\text{V}$ during the test period, the carbon filter would have increased 20% in mass by sulfur adsorption at this point. This limit was chosen based on an earlier adsorbent comparison study at Aarhus University Foulum, showing a significant breakthrough at an adsorbent weight increase between 15 and 24% [58].

3 Results

Data from three separate experiments are presented.

- Removal of H_2S from raw biogas using a biotrickling filter
- Removal of H_2S from raw biogas using a carbon filter
- Analysis of sulfur compounds at ppb_V levels at the outlet of the carbon filter

3.1 Biotrickling filter

Results from a bench-scale biotrickling filter loaded with immobilized *A. thiooxidans* are shown in Fig. 6. Oxygen in the range 0.5 to 5.0% was provided from a source of air or

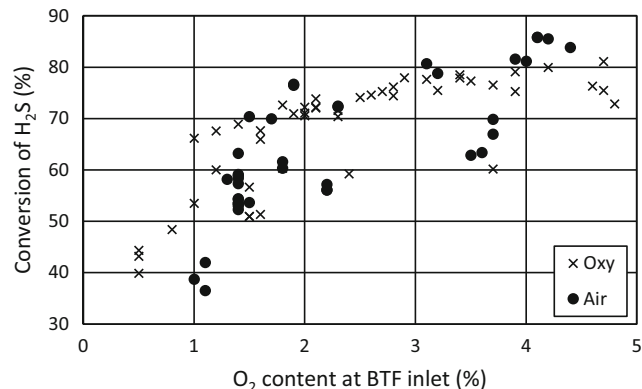


Fig. 6 Conversion of H_2S using a bench-scale BTF. Oxygen was provided by air injection or by pure oxygen

pure oxygen. In the case of air, the results show a conversion drop as the oxygen level reaches 1.0%. Operating with pure oxygen injection the BTF may be able to operate at lower O₂ surplus. However, the data contains a lot of scatter, making it difficult to clearly confirm this possibility. To obtain a reasonable conversion, an oxygen content of 2.0% is required.

3.2 Carbon filter

The performance of the carbon filter was evaluated by GC analysis during a continuous run of four cases (Table 1). The oxygen source was changed from air to pure oxygen between case 2 and case 3.

The results in Fig. 7 show successful removal of H₂S from the raw biogas by the carbon filter. Both air and pure oxygen result in efficient removal of H₂S, but in the case of air injection, a significant contamination of nitrogen is measured. Statistical analysis of the data, Table 2, shows no change in nitrogen concentration between inlet and outlet, as the *p* value is above 0.05 (it is inert). Injecting pure oxygen reduces the nitrogen contamination to an insignificant level of 400 ppm_v.

3.3 Analysis of hydrogen sulfide and other sulfur components

A chemiluminescence detector allows detection of sulfur species at ppb_v level. The analysis (Fig. 8) reveals breakthrough of CS₂ even when using newly loaded carbon (0 Nm³ biogas processed). The initial breakthrough level of CS₂ is however below 10 ppb_v. After processing of 4000 Nm³ raw biogas, the total sulfur level is around 100 ppb_v. Analysis after processing of 8000 Nm³ biogas identifies several sulfur species. Both CS₂ and DMS are found above 100 ppb_v. H₂S was not found in any of the samples. All results are assembled in Table 3.

4 Discussion

The feasibility of using pure O₂ in existing biogas treatment solutions was investigated. The H₂S removal capability of both the BTF and carbon filter was unaffected when air injection was replaced by pure O₂. This result shows how these existing technologies offer efficient bulk sulfur removal and how integration with an electrolyzer removes the current issue with nitrogen contamination. A few topics have been selected for further discussion.

Table 1 The four cases evaluated by online GC analysis

	Air	Pure oxygen
Filter inlet	Case 2	Case 4
Filter outlet	Case 1	Case 3

4.1 Oxygen requirement for hydrogen sulfide removal

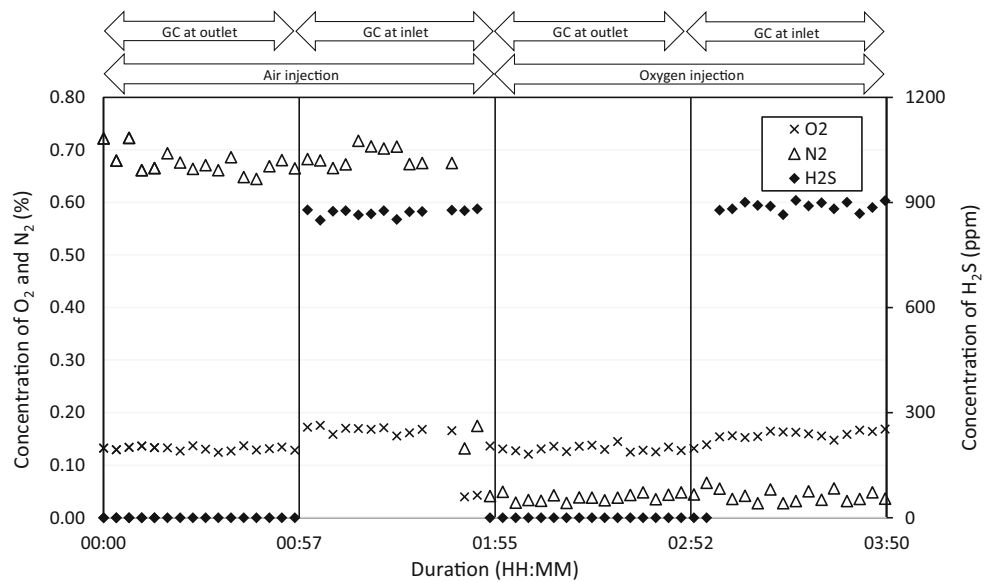
The results clearly show how air injection to the BTF cannot be an option if the biogas is to be upgraded in a downstream methanation reactor. The BTF requires significant O₂-surplus (up to 2%) before the conversion of H₂S reaches 80%. At this O₂ level, the nitrogen contamination by air injection would exceed 7%, and the gas would be unsuitable for grid export. This is a problem which was also reported by Diaz et al. [59]. However, the BTF has no problem with pure O₂ injection. With inexpensive O₂ available on-site from the electrolytic production of hydrogen, indeed the BTF may be a feasible technology for bulk H₂S removal.

The carbon filter was able to remove H₂S from an average level of 880 ppm_v to 0 ppm_v. The recommended stoichiometric O₂-surplus of 1.8 would result in an O₂ requirement of 790 ppm_v. Full conversion of H₂S would consume 440 ppm_v O₂. From Table 2, an O₂ injection level of ~1600 ppm_v is observed both in the case of air injection and in the case of pure O₂ injection. This level is above the requirement by a factor 2 and could be reduced. Because of this high level of O₂ injection, the observed N₂ contamination from air injection of 0.7% (6800 ppm_v) could potentially be reduced to 0.35%. For accurate dosing in the ppm_v range, an on-site CEM calibration should have been performed. Results in Table 2 show N₂ pass through the carbon filter as an inert, whereas the consumption of O₂ is 350 ppm_v during air injection and 250 ppm_v when injecting pure O₂. The complete oxidation of H₂S should require 440 ppm_v O₂, indicating a clear imbalance. This could be explained by a buffer effect in the carbon filter. To favor oxidation of H₂S and thiols, activated carbon can be impregnated with iodine salt as a catalyst [36, 60]. The impregnated alkaline-activated carbon used here, SolCarb KS3, is impregnated with 1–10% potassium iodide according to the material safety datasheet. The different redox states of iodine could provide the observed buffer effect. In addition, a lower initial oxygen requirement could be due to the formation of di- and oligo-sulfides, which will still strongly absorb but require less redox equivalents.

A significant reduction in N₂ contamination is observed, when the carbon filter is operated on pure O₂ (from 6800 ppm_v to 400 ppm_v). Complete removal of H₂S is observed in both cases, confirming the clear benefit of operating the carbon filter on pure O₂. The background level of N₂ in the biogas of 0.04% (400 ppm_v) is believed to be introduced with the biomass, either as air pockets trapped in the extruded straw, injected along with the manure, or as air introduced in the manure during mixing.

The electrolyzer provides a source of pure O₂ enabling replacement of air both to the BTF and carbon filter. This reduces the nitrogen contamination to an insignificant level. The BTF, in particular, does however require surplus O₂, to

Fig. 7 Analysis of O₂, N₂, and H₂S before and after the carbon filter. Oxygen was provided by air injection or by pure oxygen. Due to the GC setup, analysis of input and output could not be done at the same time. At the time of the analysis, the carbon filter would have increased 9% in mass by sulfur adsorption



uphold a high conversion of H₂S. The surplus O₂ exiting the BTF removes the need to also inject O₂ into the carbon filter. The excess O₂, not consumed by the sulfur removal steps, will react with hydrogen to form steam/water. When a sulfur guard is included in the design, a temperature increase from this exothermal reaction will be observed here. If the biogas were to contain 2% residual O₂ from the pretreatment, the additional hydrogen production, to cover both the requirements of the Sabatier reaction and the oxygen removal, would be 2.5%. This would not severely affect plant economics.

4.2 Performance of the biotrickling filter

The bench-scale BTF used in the tests was able to remove up to 80% of the total H₂S present in the biogas. This conversion is considerably lower than the reported performance of industrial filters. The BTF filter at the biogas test site at Aarhus University Foulum provides 97% conversion under stable

Table 2 Data analysis of H₂S, O₂ and N₂

Air injection			
	Inlet	Outlet	Paired t-test H ₀ : μ ₁ = μ ₂
H ₂ S	869 ppm _v ± 11 ppm _v	0 ppm _v ± 0 ppm _v	0.000
O ₂	1665 ppm _v ± 62 ppm _v	1315 ppm _v ± 47 ppm _v	0.000
N ₂	6870 ppm _v ± 177 ppm _v	6723 ppm _v ± 221 ppm _v	0.122
O ₂ injection			
	Inlet	Outlet	Paired t-test H ₀ : μ ₁ = μ ₂
H ₂ S	891 ppm _v ± 12 ppm _v	0 ppm _v ± 0 ppm _v	0.000
O ₂	1575 ppm _v ± 53 ppm _v	1325 ppm _v ± 66 ppm _v	0.000
N ₂	392 ppm _v ± 108 ppm _v	391 ppm _v ± 59 ppm _v	0.989

process conditions (local measurements not included here). Similar conversion in the range of 90–99% is also reported in literature [24, 27, 29, 32, 61, 62]. A lower overall conversion of the bench-scale BTF could be partly explained by the feed O₂ changes applied every second day during testing, providing little time for *A. thiooxidans* to achieve acclimation [62]. As such, higher conversion would be expected once

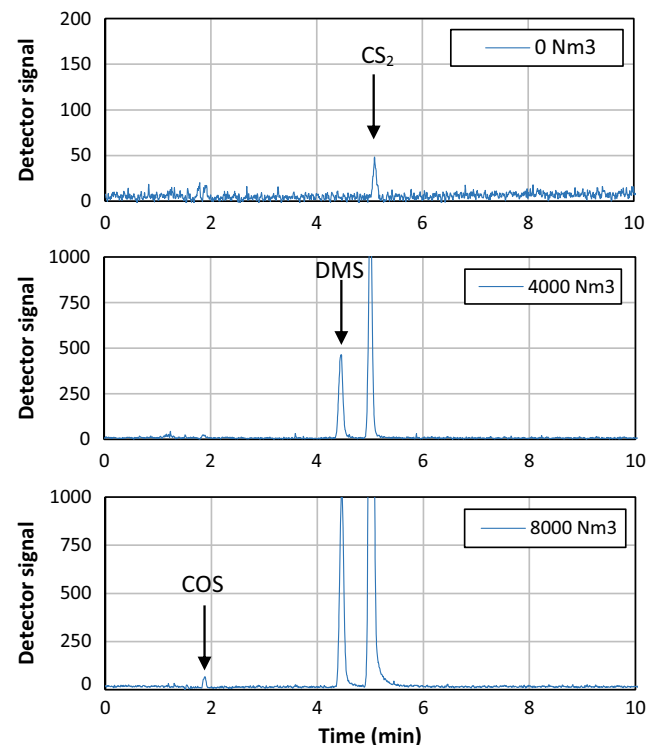


Fig. 8 Analysis of sulfur components after the carbon filter. GC spectrum of virgin carbon (0 Nm³), after treatment of 4000 Nm³ biogas and after 8000 Nm³. Retention times (min): H₂S at 1.75, COS at 1.88, DMS at 4.44, CS₂ at 5.01. H₂S below detection limit in all samples

Table 3 Analysis of sulfur components in biogas treated by impregnated alkaline-activated carbon. *BDL* below detection limit

Biogas Nm ³	H ₂ S ppb _V (retention 1.75 min)			COS ppb _V (retention 1.88 min)			DMS ppb _V (retention 4.45 min)			CS ₂ * ppb _V (retention 5.01 min)		
0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	2
4000	BDL	BDL	BDL	BDL	BDL	BDL	58	76	93	19	3	28
8000	BDL	BDL	BDL	7	14	15	131	117	113	453	408	395

*The concentration of CS₂ can only be considered as an indication. No CS₂ standard was available. The conversion to ppb_V is done by assuming a linear response to sulfur by the chemiluminescence detector (using the standard of DMS)

operational conditions have stabilized. A potential problem identified from these tests is an expected reduced conversion in case of stop-and-go operation. With fluctuating prices of electricity from PV and wind farms, stop-and-go operation of the methanation reactor could very well be expected. As desulfurization of biogas is always required, a small O₂ storage solution could be implemented, to avoid frequent changes between pure O₂ and air injection. This result highlights the need to combine the BTF with a polish step, as insufficient H₂S removal could be expected even from day-to-day plant adjustments. The cost associated with the shortened lifetime of carbon will directly couple with the performance of the BTF.

4.3 Performance of the carbon filter

The extremely sensitive chemiluminescence detector reveals insights to the performance of the carbon filter. These details are overlooked when performing analysis at ppm_V scale. H₂S is removed with very high efficiency. Even after processing of 8000 Nm³ raw biogas results show a H₂S concentration well below the detection limit of 1.5 ppb_V (Fig. 8). Assuming an average sulfur concentration of 1000 ppm_V in the raw biogas, this adsorption equals a carbon bed weight increase of 20% (200 mg sulfur/g carbon). The ability of the filter to retain other sulfur components like dimethylsulfide (DMS), carbon disulfide (CS₂), and carbonyl sulfide (COS) is clearly not as impressive. After 4000 Nm³ of biogas, a leak of DMS and CS₂ of ~100 ppb_V is observed. This is above the accepted sulfur level recommended for methanation catalyst [46–48] and clearly specifies the need for a sulfur guard before the methanation reactor. A similar pilot study (COSYMA) also observed DMS as the first sulfur species to break through the carbon adsorbent [56]. As H₂S cannot be detected in any of the samples, clearly a continuous analysis of the most predominant sulfur species, H₂S, is insufficient when evaluating carbon capacity. Often a H₂S capacity figure, with a vague breakthrough definition, will be the only benchmark available from different carbon suppliers [38]. This is clearly misleading when evaluating the risk of sulfur breakthrough. From these findings, the most important sulfur contaminant in raw biogas is CS₂. The compound is very difficult to retain with active carbon, and the concentration of ~400 ppb_V CS₂ (providing

800 ppb_V sulfur molecules) exceeds recent recommendations of max. 10 ppb_V [22] by almost two orders of magnitude!

A very interesting observation from these findings is that all the sulfur components leaking through the carbon filter (DMS, CS₂, and COS) have been reported to be removed from landfill gas and biogas from wastewater treatment facilities by filters like the BTF using *A. thiooxidans* [63–65]. Potential optimization of the biotrickling filter performance could help in the removal of these organic sulfur compounds.

4.4 Recommended design

The integration between a biogas reactor, an electrolyzer, and a reactor for catalytic methanation of biogas could be set up as shown in Fig. 9. Pure O₂ is only supplied to the BTF, and a pre-reactor/sulfur guard is included to ensure protection of the methanation catalyst from non-H₂S sulfur species.

At the solid oxide electrolyzer plus methanation demonstration unit at Aarhus University Foulum, a sulfur guard using HTZ-51 is included. This absorbent has been demonstrated to work perfectly, as there has been no change in the temperature profile of the methanator even after 1000 h of operation [66].

4.5 Contaminants not considered in this study

This study has focused exclusively on biogas from manure and straw. Although ammonia can be found in this biogas at a level of ~50 ppm_V (local measurements not included here), typical values in biogas are in the range of 10–100 ppm_V [23]. A recent study by Jurgensen et al. [67] on the impact of ammonia on methanation catalysts specifically concludes that the removal is unnecessary. In fact, at a level of 100 ppm_V, ammonia showed some benefits like reduced coke formation and a lower deactivation rate on methanation catalysts. The maximum limit of 10 ppm_V ammonia in the final gas (European Norm 16,723:2016) will not be a concern, as ammonia would be subject to cracking in the methanation reactor.

Unlike biogas from farm sites, studies on landfill gas and biogas from wastewater treatment facilities often show significant amounts of siloxanes, halogenated hydrocarbons, and other volatile organic compounds (VOCs). Siloxanes are organic silicon compounds found in products like cosmetics,

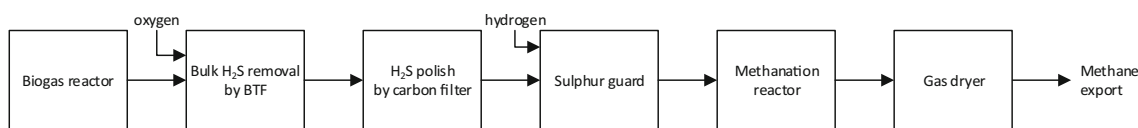


Fig. 9 The recommended setup to allow integration between a biogas reactor, an electrolyzer, and a catalytic methanation reactor. Hydrogen and oxygen are provided by electrolysis

detergents, and pharmaceuticals. Both cyclic and linear siloxanes are found in landfill and biogas [31]. Highest levels are found in biogas from wastewater treatment facilities, and thermophilic digesters seem to struggle with the highest levels [68]. The problem with siloxanes is the formation of inorganic SiO_2 deposits inside gas burners causing clogging [69]. A successful removal method is the carbon adsorbent C64 from Airdep installed at the wastewater treatment facility of Collegno, Italy [70]. A second verified option is the carbon adsorbent Bi-On-AC from Bioconservación installed at the Mataró wastewater treatment facility northeast of Barcelona, Spain [31]. Both wastewater treatment facilities convert the produced biogas to electricity using solid oxide fuel cells. As such, this application is extremely sensitive to siloxanes [71].

Landfill gas often contains the highest levels of halogenated hydrocarbons. Possible sources are discarded refrigerants, plastic foams, and paints. Chlorine is the most abundant halogen species. Besides high levels of halogenated hydrocarbons, landfill gas is also the gas containing the highest levels of VOCs [23, 68]. Both chlorine and VOCs will affect the performance of the methanation catalyst [22]. VOCs are also shown to significantly reduce the capacity of other adsorbents like the adsorbent for siloxanes removal [72]. As landfill gas also contains significant amounts of N_2 and O_2 from ingress of air, utilizing landfill gas as a CO_2 source for catalytic methanation seems less attractive, as custom gas treatment solutions will be required at each site.

5 Conclusion

To enable catalytic methanation of CO_2 directly in biogas, the performance of a bench-scale biotrickling filter and a carbon filter was evaluated. Current issues with nitrogen contamination from these processes were reduced to insignificant levels, when the filters were operated using pure oxygen. Although hydrogen sulfide was efficiently removed in the carbon filter, analysis at ppb_v level revealed several sulfur compounds leaking through this last treatment step. These critical sulfur contaminants of raw biogas were found to be carbon disulfide (CS_2), dimethyl sulfide (DMS), and carbonyl sulfide (COS). A sulfur level at two orders of magnitude above the recommendation for methanation catalyst was found. To avoid issues with sulfur poisoning of the methanation catalyst, a sulfur guard needs to be included in the final design of combined electrolysis–methanation plants.

The technologies selected for treatment of raw biogas are all proven in full scale. The integrated system can be build today serving as a stepping-stone towards a fossil-free future. Solutions utilizing CO_2 as a resource have vast potential in current and future energy systems.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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