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Selected Methods of Advanced Biogas Upgrading

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The upgrading of biogas for the production of biomethane to be injected to the natural gas grid has gained significant importance in recent years. It is often considered to be superior to the production of electricity and district heat with internal combustion engines mainly because of better energy utilisation, higher flexibility and beneficial economic prospects. Biogas upgrading is commonly accepted as state-of-the-art and a considerable number of small and industrial scale plants have been commissioned to date representing the portfolio of currently available upgrading technologies. Nevertheless, academic research clearly demonstrates that still a huge potential for optimisation and development is existing in this field.
The current work contributes to the field of biogas upgrading by suggesting innovative and powerful approaches along the whole process chain. The importance of trace component separation is exemplary depicted by introducing a novel desulphurization technology based on chemical-oxidative scrubbing applying an innovative short-contact-time apparatus. Thus, separation efficiency for hydrogen sulphide is maximized while the simultaneous separation of carbon dioxide is minimized to assure minimum chemicals consumption. As an example for the major biogas upgrading step of carbon dioxide removal, the process of membrane-based gas permeation is suggested. This technique stands out for its excellent adaptability regarding biomethane quality and methane recovery already during the design phase, simple and robust plant operation, low specific energy demand as well as reasonable upgrading costs. Finally, a combination of biogas upgrading with the Power-to-Gas approach is presented. This process provides the possibility of storing renewable electrical excess energy in form of biomethane in the high-capacity natural gas grid, an overall increase of biomethane output of a given biogas plant by maximizing carbon utilization and a reduction of the specific carbon footprint of a biomethane site.

1. Introduction

A considerable amount of contemporary research is focussed on renewable and sustainable supply of energy for society without depletion of fossil resources and without surplus emissions of greenhouse gases. It is anticipated that not a single source of alternative energy but a mix of various energy sources and carriers will contribute to the energy system of the future. Beside continuously rising PV and wind power sources which usually own highly fluctuating and hardly predictable production, biomass energy conversion techniques capable of base load and balancing energy operation will cover a decent share in future non-fossil energy scenarios (Pöschl et al., 2010).
Amongst biomass-based energy sources, the utilization of biogas plays an important role both on European and worldwide scales. It is estimated that the biogas share in the contribution of bioenergy to EU-28 renewable energy targets by 2020 will be in the range of 25 %. On a global perspective, power generation capacities from commercial biogas facilities are expected to rise from 14.5 GW in 2012 to 29.5 GW in 2022 (Sun et al., 2015). A recent assessment of biogas production in Europe (Wellinger, 2015) estimates a total number of biogas plants operative in the range of 14,500 with an installed electric capacity of roughly 7,900 MW. Typical substrates for contemporary biogas plants are energy crops (e.g. maize), catch crops (Shahzad et al., 2014), agricultural residues (e.g. leaves and stems), wastes from agro-industry and food processing, collected municipal bio-waste, animal manure and sewage sludge from aerobic wastewater treatment

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(Weiland, 2010).Biogas produced from anaerobic digestion processes mainly consists of methane (CH_4), carbon dioxide (CO_2) and water vapour (H_2O) (Weiland, 2010). Minor components of raw biogas include nitrogen (N_2) and oxygen (O_2) from air, hazardous components like ammonia (NH_3) and hydrogen sulphide (H_2S)(Sun et al., 2015). Depending on the feedstocks further pollutants like siloxanes or VOCs (fatty acids, terpenes, alcohols) have to be considered. Biogas from landfills additionally contains components like chlorinated or fluorinated hydrocarbons, heavy metal vapours or higher hydrocarbons (Rey et al., 2013).

Considering the various utilization pathways of biogas energy content like generation of heat (process heat, district heat), generation of power (CHP gas engine, micro gas turbine, Stirling engine, fuel cell) or biogas upgrading (natural gas grid injection, locally available CNG fuel) pointed out in a review article by Pöschl and co-workers (Pöschl et al., 2010), the latter pathway is considered superior by numerous authors because of better energy utilization (Sun et al., 2015) and higher flexibility (Makaruk et al., 2010). The process of biogas upgrading includes the removal of bulk contaminant CO_2 as well as the removal of trace components (like NH_3, H_2S), gas drying and compression to end up with a biomethane product gas stream characterised by a methane content of typically more than 95 % (Niesner et al., 2013) and very low levels of hazardous contaminants (typically lower than 5 ppmv) (Harasek, 2015).

As trace components are often harmful to downstream processing units, the removal of NH_3, H_2S and siloxanes is usually the first upgrading step (typically after initial pressure increase). While NH_3 is quantitatively separated during cryogenic moisture removal followed by an activated carbon adsorption (which can also be designed to completely remove siloxanes), the separation of H_2S is reported to be conducted in several ways (Miltner et al., 2012). Depending on the initial content of H_2S in the raw biogas processes like sulphur precipitation (in the fermenter), ex-situ biological desulphurization (in a separate scrubbing column) or adsorptive desulphurization (on metal oxides or activated carbon) are frequently applied. Recently, a process of chemical absorption using EDTA for combined H_2S-CO_2-removal has been presented (Schiavon Maia et al., 2014). A novel process based on chemical-oxidative scrubbing for an efficient and economic sulphur removal for various gaseous energy carriers is presented in the current work.

Concerning the main step of biogas upgrading, CO_2 removal, a number of technologies are readily available on the market that have already proved their technical feasibility, robustness and economic operation. Amongst these are pressurized water scrubbing, chemical scrubbing (MEA, DEA, MDEA, piperazine), physical scrubbing (Selexol©, Rectisol©, Genosorb©), adsorption (PSA, TSA) and membrane-based gas permeation (Niesner et al., 2013). The flexibility and adaptability of gas permeation process will be presented in detail in the current work.

2. Biogas desulphurization using chemical-oxidative scrubbing

The absorption of H_2S in caustic solutions is one of the oldest methods for gas desulphurization. The herein presented novel method utilizes sodium hydroxide as a caustic and the pH is carefully adjusted to maximize absorption selectivity of H_2S over CO_2 (Miltner et al., 2012). Taking advantage of the different absorption kinetics of H_2S and CO_2 in caustic solutions allows for a further increase of absorption selectivity. Absorption of H_2S is distinctively faster than absorption of CO_2 leading to a design of the contact apparatus with minimum contact time between scrubbing solution and gas phase. A process flow diagram of this novel desulphurization process is given in Figure 1. The scrubbing liquid is distributed in the gas stream as a fine spray, intensely mixed by static mixing elements and subsequently separated from the gas by coalescence. The caustic scrubbing liquid is loaded with H_2S(aq) and discharged to an oxidation chamber via a gastight siphon.

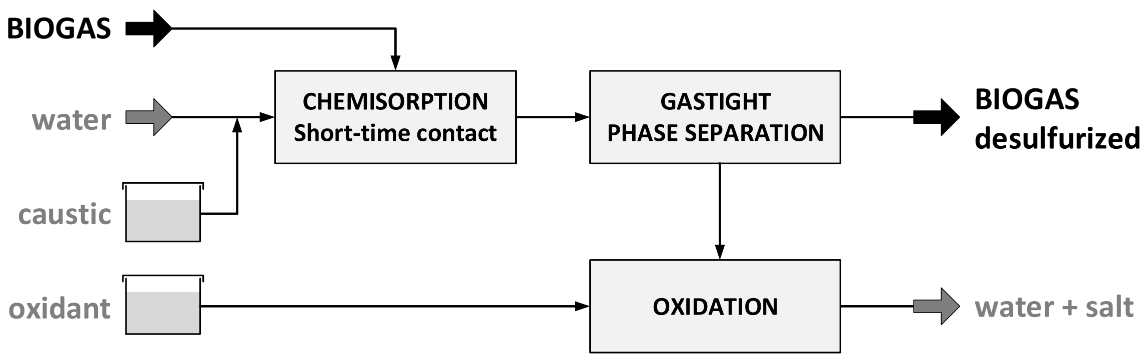

Figure 1: Process flow diagram of chemical-oxidative biogas desulphurization with short-time contact apparatus

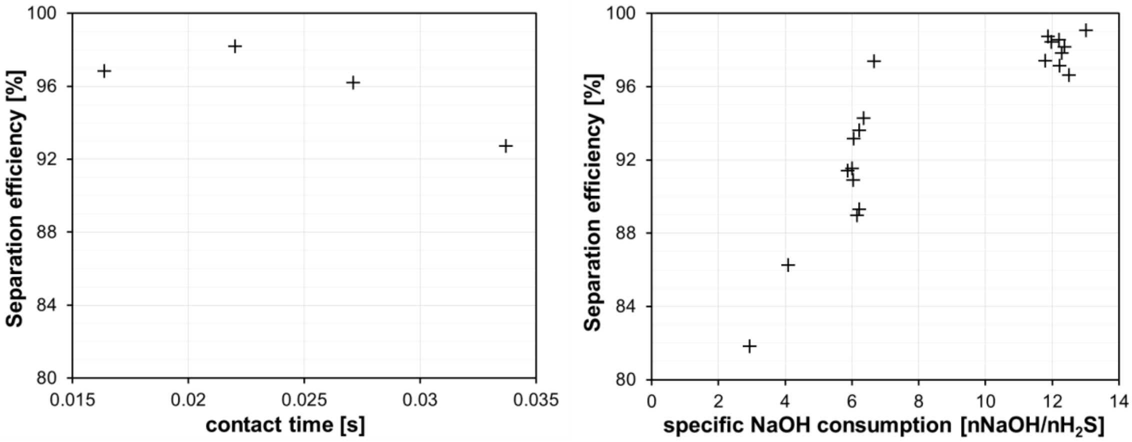

Figure 2: Separation efficiency of single-step desulphurization vs. contact time and caustic consumption

In the oxidation step $H_2S(aq)$ is oxidised to elemental sulphur, sulphite (preferential) or sulphate depending on the content of oxidizer used, usually hydrogen peroxide (H_2O_2). Thus, $H_2S(aq)$ is removed from the absorption equilibrium which further increases the selectivity of H_2S over CO_2. As a result, only a minimum of CO_2 is separated during desulphurization leading to a very low consumption of caustic to maintain the desired pH.
The novel desulphurization process has been used to construct a single-staged pilot plant designed for a raw biogas capacity of 200 m³/h (STP) that has been operated at a biogas/biomethane plant in Austria for two months. Sensitivity analysis for structural and operational variations (spray nozzle, contacting area, liquid-gas-ratio, contact time) as well as an experimental parameter optimization have been performed. As a result, Figure 2 depicts achievable H_2S separation efficiencies as a function of contact time and specific caustic consumption. It is obvious that low contact times (20 to 25 ms) are favourable for removal efficiency as long as the gas/liquid mixing quality is maintained. Furthermore, it is concluded that a convenient control of removal efficiency and H_2S content of the sweetened gas can be realized through variable caustic supply (variation of pH) providing a value of more than 92 % even at a modest NaOH consumption of 6 mol/mol. Assuming a proper oxidation chamber design, the consumption of oxidizer is an exclusive function of H_2S absorbed.Analysed results strongly suggest the development of a multi-staged concept to further reduce consumption of chemicals and fresh water. Consequently, a three-staged demonstration plant designed 500 m³/h (STP) raw biogas with an initial H_2S content of 1,000 ppmv has been designed and constructed. The plant is scheduled to start operations mid 2016 at a German biogas/biomethane site. Results from this operation will be used for a final optimization, assessment of economic characteristics and a full commercial rollout.

3. Biogas upgrading using membrane gaspermeation

The application of membrane-based gaspermeation for the upgrading of biogas for biomethane production has gained increasing importance especially during the last decade. The technology is commercially available and provided by plant constructors and membrane companies. The robustness and economic benefits connected to this technology have been shown by a remarkable number of operational plants. Nevertheless, substantial technological and operational improvements within the application of membrane-based biogas upgrading are still implemented. Three different biogas upgrading plants based on gaspermeation are depicted in Figure 3. The principle of gaspermeation is based on different solubilities and diffusivities of gas constituents in a given membrane material, typically of polymeric type for biogas upgrading. By providing a driving force for separation in the form of partial pressure difference between the two sides of the membrane quantitative separation of gas components is performed. Relatively low permeabilities of molecules through dense polymeric layers lead to the requirement of comparatively large membrane surface areas. By reason of highest packing density, most membrane manufacturers nowadays provide hollow fibre membrane modules for gaspermeation even though other construction variants like envelope-type are still of high relevance.
A highly interesting aspect in gaspermeation arises from the possibility of combining different membrane materials featuring different separation characteristics in a single gas upgrading process. Membrane material combination allows for the consecutive and largely separated removal of different gas constituents in a single step. A theoretical elaboration of the combination of glassy and rubbery polymer materials for the combined removal of CO_2 and H_2S from raw biogas based on a simulative approach has recently been published by Makaruk et al. (2013).

Figure 3: Three different membrane-based biogas upgrading plants (left: Bruck/Leitha in Austria ; mid: Wr. Neustadt in Austria; right: Kisslegg in Germany)

The high modularity of membrane technology allows for an unrivalled adaptability of an upgrading plant design to individual process needs. The total membrane area can easily be adjusted by adding or removing individual membrane modules if these are proper sized. A vast number of plant topologies involving several membrane stages, internal and external recycle flows, several compression and recompression stages as well as intermediate expansion can be developed and analysed for maximum energy efficiency or minimum total upgrading costs (Makaruk et al., 2010). A well-structured parameter variation and optimization involving different topologies like in this case for biogas upgrading necessitates a simulation tool with rigorous model description and powerful multidimensional optimizer. Such tool has been introduced by Makaruk and Harasek with a special emphasis on biogas upgrading (Makaruk et al., 2009). To illustrate the effect of topology and design on the performance of real biogas upgrading plants Table 1 summarizes operational characteristics of three different membrane-based biogas upgrading sites in Austria.

Table 1: Operational characteristics and performance parameters of differently designed membrane-based biogas upgrading plants in Austria (same plant manufacturer)

plant layout (membrane stages)	CH_4 recovery [%]	CH_4 content in offgas [%v/v]	specific power demand for upgrading [kWh/m³$_{STP}$ raw biogas]	specific upgrading total costs (1000m³/h biogas) [€/m³$_{STP}$ biomethane]	source
1 stage	80.0	23.5	0.12	11.2	(Miltner et al., 2009)
2 stages	95.0	7.2	0.20	13.1	(Miltner et al., 2008)
4 stages	99.5	0.8	0.26	14.6	(Harasek, 2015)

The most important factor in this analysis is the adjustable CH_4 recovery and thus the content of this species in the offgas stream. Single staged upgrading reaches the desired biomethane quality with low efforts concerning electrical power consumption and specific costs. The huge drawback is the considerable amount of methane lost to the offgas which is based on the mediocre recovery value. A proper offgas treatment, mostly in terms of combustion and heat utilization, is absolutely mandatory. On the other hand, when considering a sophisticated state-of-the-art membrane arrangement, significantly higher recovery can be reached resulting in a very low CH_4 content in the offgas, which subsequently is eligible by law to be vented to the atmosphere even without any further treatment. This higher recovery is at the expense of higher electricity demand for gas compression and slightly increased specific upgrading costs. This flexibility and adaptability of a gas separation technology already during the first design steps together with the robustness and ease of operation lay the foundation of the remarkable effectivity of gas permeation to the field of biogas upgrading.

4. Biogas upgrading combined with Power-to-Gas approach

During biogas upgrading a considerable amount of renewable carbon is separated from the biomethane product in form of CO_2. Provided that state-of-the-art technologies are used, this offgas-stream is characterized by high content of CO_2 with only minor contamination of CH_4, H_2O, N_2 or others. The utilization of this separated carbon to further enhance biomethane output would be advantageous regarding the overall material balance and the biomethane-specific carbon footprint of the installation. Thus, from a systemic point of view, CO_2 utilization and conversion to CH_4 would increase the sustainability of this biomethane approach.
The concept of Power-to-Gas (PtG) includes the production of gaseous energy carriers from electric energy, typically renewable excess energy from PV or wind power sources (Götz et al., 2016). The idea focusses on long-term storage of electric energy in existing infrastructure, reduction of peak loads in electric grids, and the production of vehicle fuels from electricity.

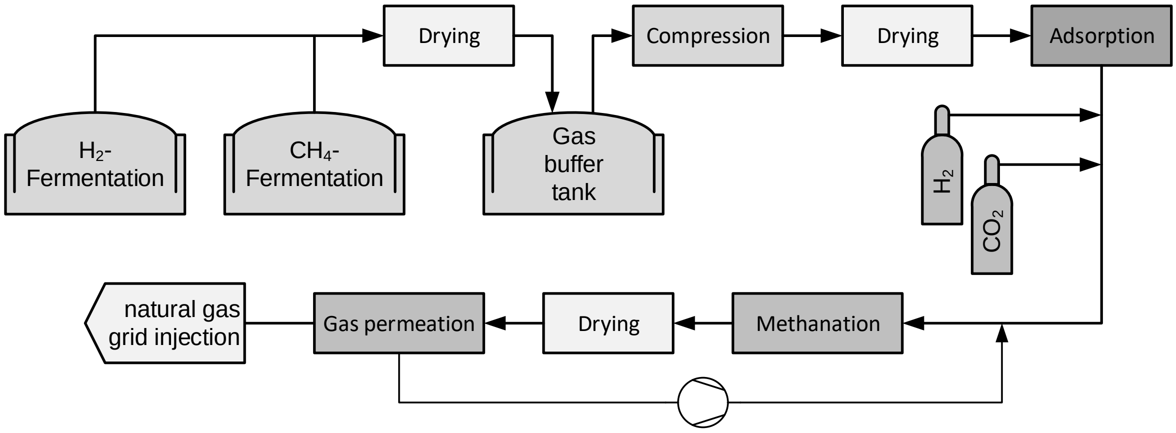

Figure 4: Pilot plant layout for the demonstration of the developed Power-to-Gas-concept

Electric power is used to produce hydrogen via electrolysis (alkaline or PEM) either on fluctuating or base-load scenario. Hydrogen can directly be used as a desired energy carrier (vehicle fuel, injection to natural gas grid to a certain extent) or it can be used to produce methane by reaction with CO or CO_2 as a carbon source (Schiebahn et al., 2015). This process is called methanation and can be realized by biochemical conversion (in-situ bio-methanation in biogas fermenter, ex-situ bio-methanation in distinct bioreactor) or thermo-catalytical conversion (Sabatier-process in heterogeneously catalysed reactor). After a final gas upgrading the product gas from methanation is permitted to be fed into the natural gas grid without admixing restrictions.

Biogas is considered to be a favourable carbon source for PtG-concepts and consequently, biogas upgrading plants are expected to be suitable sites for PtG-implementations (Götz et al., 2016). An already existing biogas upgrading plant might additionally be used for the upgrading of the methanation product gas and the segregated CO_2 stream acts as carbon source for the PtG-process. Two basic process layouts regarding the arrangement of the main gas upgrading might be distinguished: i.) separation of CO_2 from biogas and utilization of the pure stream in methanation and ii.) methanation of the complete (pre-cleaned) biogas stream. Either way, the application of gaspermeation with polymeric membranes promises to show outstanding performance during the required gas separation tasks. In addition to the high separation selectivity for the separation of CH_4/CO_2 in biogas upgrading most membrane materials show even higher selectivities for the removal of H_2 from CH_4. As a result, one and the same membrane-based gas upgrading plant can be used both for the biogas upgrading and for the removal of unreacted educts in the methanation product gas. This is essentially interesting for a hook-on to existing plants to extent the biogas upgrading operation with a PtG-mode (Harasek, 2015).

A pilot plant has been designed to demonstrate and analyse named biogas/PtG-concept on a scale of 1 to 5 m^3_{STP}/h. This plant comprises combined biogas and hydrogen dark fermentation, compression, adsorption for trace component removal, methanation and membrane-based gas upgrading. A scheme of the pilot plant layout is given in Figure 4. Said plant has been operated under real-world conditions for several weeks in 2015. Results and findings are presented in a separate work (Kirchbacher et al., 2016).

5. Conclusions

Biogas upgrading for the production of biomethane, either for natural gas grid injection or as a local renewable CNG-fuel, is well-known state-of-the-art and a multitude of different technologies are commercially available. Nevertheless, academic research clearly demonstrates that still a huge potential for optimisation and development is existing in this field. Additionally, numerous studies indicate the high significance of the biogas sector within the portfolio of renewables in a sustainable energy system. Many authors point out that biogas upgrading is preferable over direct power generation mainly due to better energy utilisation and higher flexibility. Furthermore, many existing biogas plants have to deal with expiring or not cost-covering green energy feed-in tariffs for electricity and the marketing of biomethane would increase the overall profitability of the plant investment.

The current work contributes to the field of biogas upgrading by suggesting innovative and powerful approaches along the whole process chain. A novel process for biogas desulphurization based on chemical-oxidative scrubbing in a short-time contacting device has been introduced. This robust technology provides a stable single-step-removal-efficiency of more than 95 % even for highly fluctuating raw biogas sulphur freights and is completely automatable. Membrane-based gaspermeation has been presented as a highly interesting process alternative to other biogas upgrading techniques already well-known on the market. It has been shown that process layout is easily adaptable, plant operation is simple and robust and specific energy demand and total upgrading costs are highly competitive. Finally, a combination of biogas upgrading with a Power-to-Gas approach has been discussed that allows for an increase of biomethane output and an improvement of the specific carbon footprint of a given biogas plant.

It is expected that the application of innovative and advanced methods of biogas upgrading facilitates the economic and ecologic performance of existing or newly constructed biogas/biomethane plants. Thus, the biogas sector could be empowered to contribute significantly and reliably to a sustainable energy system of the future.

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