Removal of Oxygen from Biogas via Catalytic Oxidation of Methane

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Abstract

In this work, the utilization of methane as a reducing agent for oxygen in a catalytic process for oxygen removal was examined in comparison with state-of-the-art technologies for this task. Therefore fundamental examinations on catalytic activity, reaction kinetics, catalyst materials and reducing agents for oxygen have been carried out. On the basis of these results, process economics were evaluated and recommendations on the application of catalytic processes for the removal of oxygen are given. Besides the evolved data on operating conditions and process design, results of a first field test with biomethane as feed gas are briefly summarized.

1. Introduction

In Europe biogas features a strong growth. In Germany approximately 150 biogas injection plants are in operation [1]. On the way towards a further increase of the overall biogas capacity in Europe, a certain level of biogas injection will be reached, which demands either recompression of upgraded biogas from local gas distribution networks or the intensification of its direct injection into transportation networks (see Figure 1).

In recent biogas monitoring programs [2, 3] oxygen contents in the range of 0.1 vol.-% up to 1.8 vol.-% have been reported in upgraded biogas. The average oxygen content was 0.5 vol.-%.

In order to protect the gas infrastructure in general from corrosion and especially the gas storage systems from deposition of elemental sulfur [4 - 6], a threshold value for oxygen of 10 ppmv for transport pipelines (MOP > 16 bar) connected to underground storages or cross border transmission has been set up [7, 8]. Since a small amount of oxygen in biogas is inevitable, a process for oxygen removal has to be integrated into the biogas purification chain [9].

One promising alternative to state-of-the-art technologies is the catalytic oxidation of methane [9]. Up to now, there has been no considerable technical relevance for the catalytic removal of oxygen as a trace compound from a gas stream with methane as major component. Traces of oxygen are usually removed by adsorption based processes (e.g. on Cu, Cr) or by oxidation of hydrogen. The typical amount of oxygen in biogas exceeds the threshold value for economical application of adsorption based processes. The major drawback of hydrogen is that it has to be added to the biogas stream from external, in general fossil sources, which has a negative impact on process sustainability. Besides, oxidation of methane appears to be the economically and technically preferred option [9].
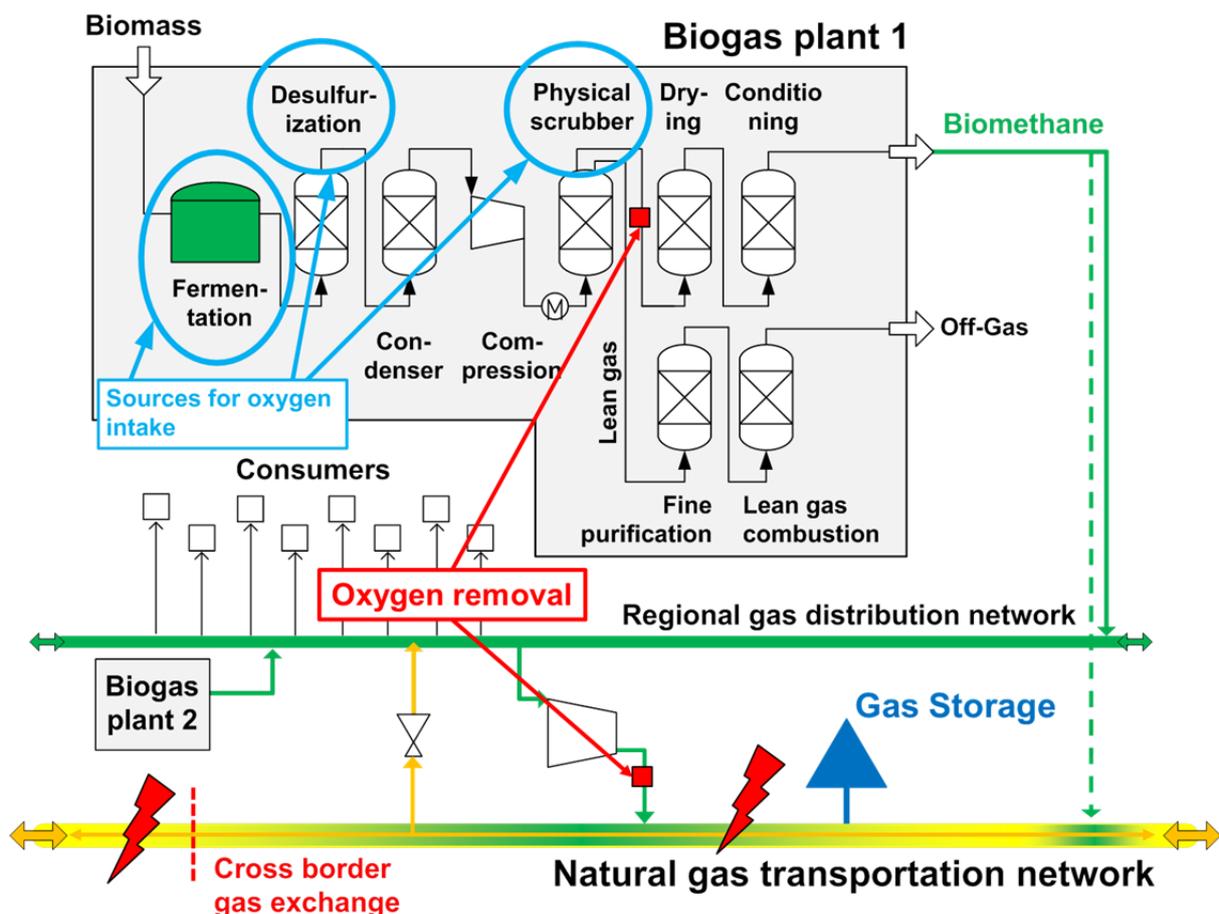
Fig. 1: Overview over a typical biogas plant setup, points of oxygen intake and spreading of the oxygen load in the gas grid infrastructure (■: possible installation points for O_2-removal units)

2. State-of-the-art technologies for oxygen removal

There are several ways to remove oxygen from gas streams. Besides some physical processes, such as adsorption on molecular sieves or activated carbon, membrane separation or certain cryogenic solutions, which are able to remove oxygen, when present in high amounts, exclusively chemical processes are suitable to meet the requirements of a residual oxygen content of 10 ppmv. This is due to the fact that physical processes require a distinct concentration gradient, which is comparatively small in the case of the removal of oxygen from biogas, prohibiting any physical process to become economically feasible [9].

However some chemical processes are commercially available and can be regarded as state-of-the-art technologies. There are two general options. The first is a continuous adsorption based process, commonly using copper (eq. 1) or chromium as adsorption materials. Some younger approaches focus on ferrous adsorption material for this task. In any case, the adsorption material is placed in at least two or more fixed-bed adsorption columns, necessary for alternating operation of loading and regeneration (see Figure 2).

$$2\ Cu + O_2 \rightarrow 2\ CuO \qquad\qquad \Delta_R H^{\ominus} = -316\ kJ/mol \qquad\qquad (1)$$

For regeneration of the adsorbent, a reducing agent is required. Usually hydrogen is applied (eq. 2), which is not available at biogas plants and therefor has to be provided from an external source.

$$CuO + H_2 \rightarrow Cu + H_2O \qquad\qquad \Delta_R H^{\ominus} = -129\ kJ/mol \qquad\qquad (2)$$

For copper based adsorption processes a minimum operation temperature of 150 °C needs to be maintained. The maximum temperature is limited to 250 °C in order to avoid thermal damage of the bed material. As a result of the strong exothermic oxidation reaction, the oxygen amount in the feed gas is limited to 1 vol.-%.

In addition to this limitation, the oxygen uptake capacity of commercially available adsorbents is comparatively low. For these reasons, such processes are typically applied to protect oxygen sensitive systems in the context of fine purification where low oxygen contents (<< 0.1 vol.-%) are present in the feed gas [10 - 12].
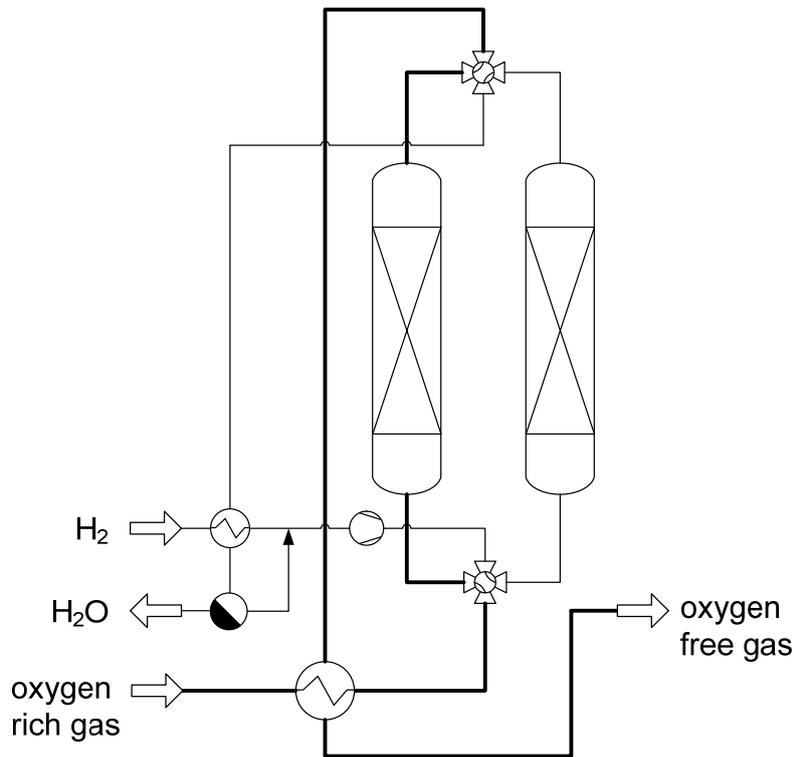
Fig. 2: Flow scheme of an adsorption based process for oxygen removal

The second commercially available option is a heterogeneously catalyzed oxidation reaction of either hydrogen or hydrocarbons to form water and carbon dioxide as products (eqs. 3, 4) [12, 13], respectively. Fig. 7 shows a technical implementation.

$$2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(l)} \qquad\qquad \Delta_R H^\ominus = -571{,}6\ \text{kJ/mol} \qquad (3)$$

$$C_nH_{(2n+2)} + (1.5n+0.5)\ O_2 \rightarrow n\ CO_2 + (n+1)\ H_2O_{(l)} \qquad\qquad (4)$$
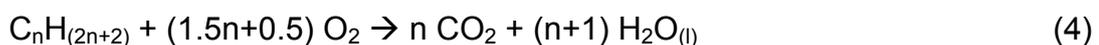
The advantage of hydrogen (eq. 3) is that the reaction can be operated at low temperatures (of about 80 °C) when it is catalyzed by noble metals such as platinum or palladium [12].

While methane is the major gas component, many natural gases contain hydrocarbons, like ethane, propane or butane. In case of biogas, LPG or propane are used for adjustment of the calorific value before injection into the natural gas grid [10]. These hydrocarbons can also be used for catalytic oxygen removal. In case of hydrocarbons higher reaction temperatures as required for hydrogen, typically ranging from 200 °C to 300 °C, have to be applied [14]. The corresponding heats of combustion for hydrocarbon fuels (eq. 4) are noted in Table 1 [14].

Tab. 1: Enthalpies of combustion for total oxidation of different fuel gases

$\Delta_R H^{298K}$	CH_4	C_2H_6	C_3H_8	C_4H_{10}
kJ/mol	- 890,5	- 1560	- 2220	- 2877

In both cases, the reaction is performed in a fixed-bed configuration. Besides the catalytic reaction unit, only one single heat exchanger for feed gas preheating is necessary. As long as the oxygen content in the feed is high enough and insulation of the process is adequate, the adiabatic temperature increase of about 10 - 16 K per 0.1 vol.-% of oxygen (in a typical biogas mixture) is sufficient to allow for an autothermal operation mode. In such a case an electric heating system is only necessary during the start-up period. As a catalyst is applied for this reaction, minor constituents like sulfurous gases components, siloxanes or halogenated compounds need to be taken into consideration.

3. Oxygen removal by oxidation of methane

A new approach is the implementation of the catalytic oxidation of methane as an oxygen removal process (eq. 5). Certainly, the oxidation reaction of methane is widespread in industry and has been under intensive research for decades. The actual challenge is the present gas composition with its very low oxygen content in comparison with typical industrial applications, such as exhaust gas purification by catalytic post-combustion of CH_4 traces with excess oxygen. Up to now, there is nearly no technical relevance in industry for catalytic oxidation units, operating in excess fuel conditions.

$$CH_{4(g)} + 2\,O_{2(g)} \rightarrow CO_{2(g)} + 2\,H_2O_{(l)} \qquad \Delta_R H^\ominus = -890{,}5\ kJ/mol \qquad (5)$$
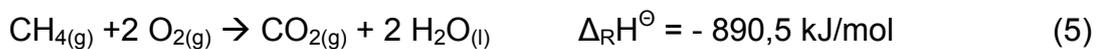
The total oxidation of methane as a gas purification step offers some advantages, as methane is available at high concentrations in biogas and the fuel demand of the reaction is comparably low (4 times lower than in the hydrogen case). Furthermore, reaction products of the methane oxidation reaction are treated in the biogas purification process anyway and the utilization of bio-methane is the more sustainable option, as compared to hydrogen or hydrocarbons from fossil sources.

In order to examine the reaction under the given fuel rich conditions, a lab scale catalytic test rig was built. Key aspects of the experiments were the determination of kinetic data for a set of reference catalysts on noble metal basis. For comparing operating temperatures, some alternative fuels and catalysts were also tested. Afterwards, the process was demonstrated with biogas from an injection plant, focusing on the influence of trace compounds on catalyst durability. On basis of these results, process performance and economics were compared for different fuels and typical oxygen contents in biogas.

4. Experimental set-up

The lab-scale apparatus for determination of the reaction kinetics consists of a gas-mixing unit, a reactor with an electrical furnace and a gas analyzer unit (see Figure 3). The fixed bed reactor (1.4541 stainless steel) is divided into a preheating and a reaction zone. After leaving the reactor, the product gas composition is analyzed by a micro-GC (Agilent Technologies, Inc.) and an electrochemical oxygen transmitter (Pro-Chem-Analytik GmbH).
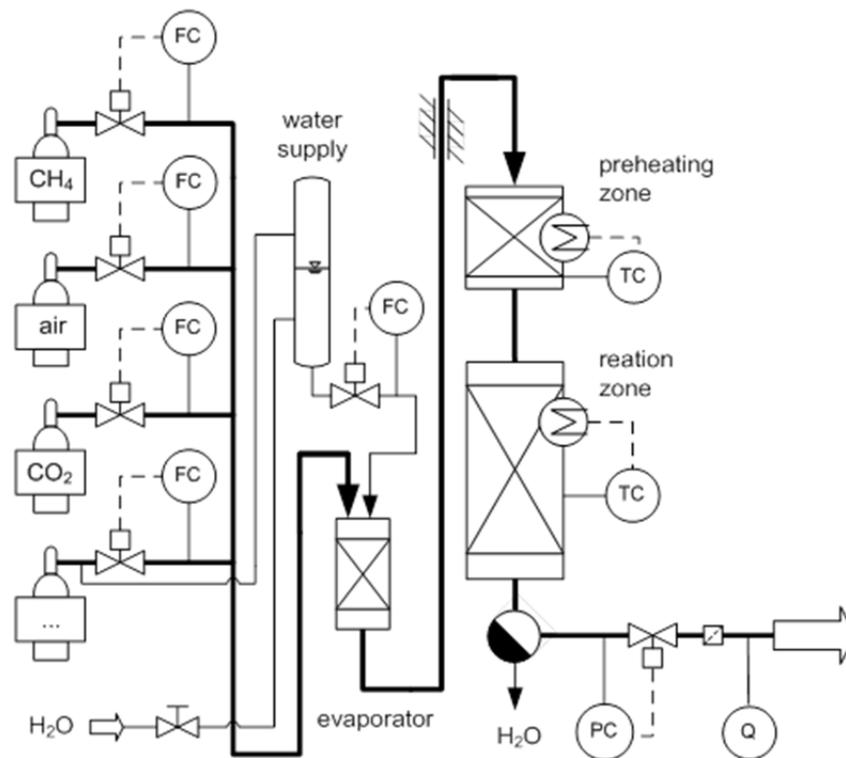
Fig. 3: Flow scheme of the experimental setup used in this work

5. Results and discussion

Some of the results are given in Figure 4 [10], which shows a variation of the oxygen content in a range of 0.1 vol.-% to 0.8 vol.-% (blue curves) in methane with a variation of operation pressure from 1 bar to 10 bar (red curves) for a platinum catalyst. As a typical behavior, it can be observed that an increase of oxygen content in the feed gas results in a higher temperature, necessary for the desirable complete conversion of oxygen for a given GHSV of 45.000 h^{-1}. At ambient pressure, this temperature ranges between 250 °C and 350 °C.

In contrary, when traces of methane are to be removed from air streams, a minimum of 350 - 400 °C is usually required with a platinum catalyst. Taking into account the

variation of pressure leads to the conclusion, that the methane partial pressure in the gas has a crucial impact on the reaction rate - which seems surprisingly at first as methane is available in large excess.
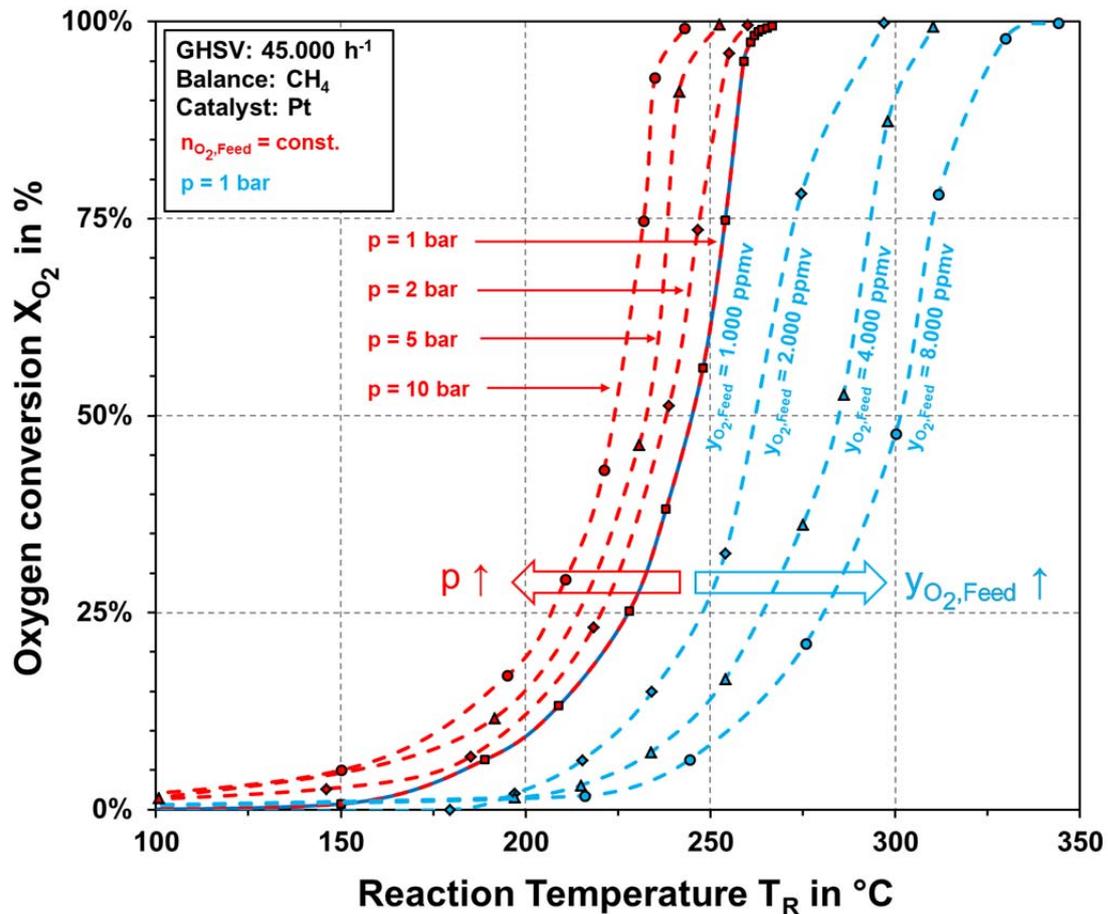
Fig. 4: Oxygen conversion in the lab scale test rig at Engler-Bunte-Institute as a function of feed composition and system pressure

In literature the reaction mechanism for the oxidation of methane is described by the so called Eley-Rideal mechanism [15, 16], which indeed assumes methane to have a limiting influence on reaction rate due to weak absorption interactions with the catalytic surface. Eley-Rideal presumes oxygen to be sufficiently absorbed on the catalytic surface at any time. However, these observations are based on examinations performed in excess of oxygen. On the basis of the experiments carried out in this work, the validity of Eley-Rideal mechanism for the oxidation of methane can be extended to partial pressures of oxygen as low as approximately 0.1 mbar.

In addition to the examinations with methane, a variation of fuel gases was carried out. As an overview, Figure 5 shows the relative stability of the potential fuel components for oxygen removal. For reasons of comparison, the fuel gas content in the feed gas was defined to 0.25 vol.-% for all fuels.
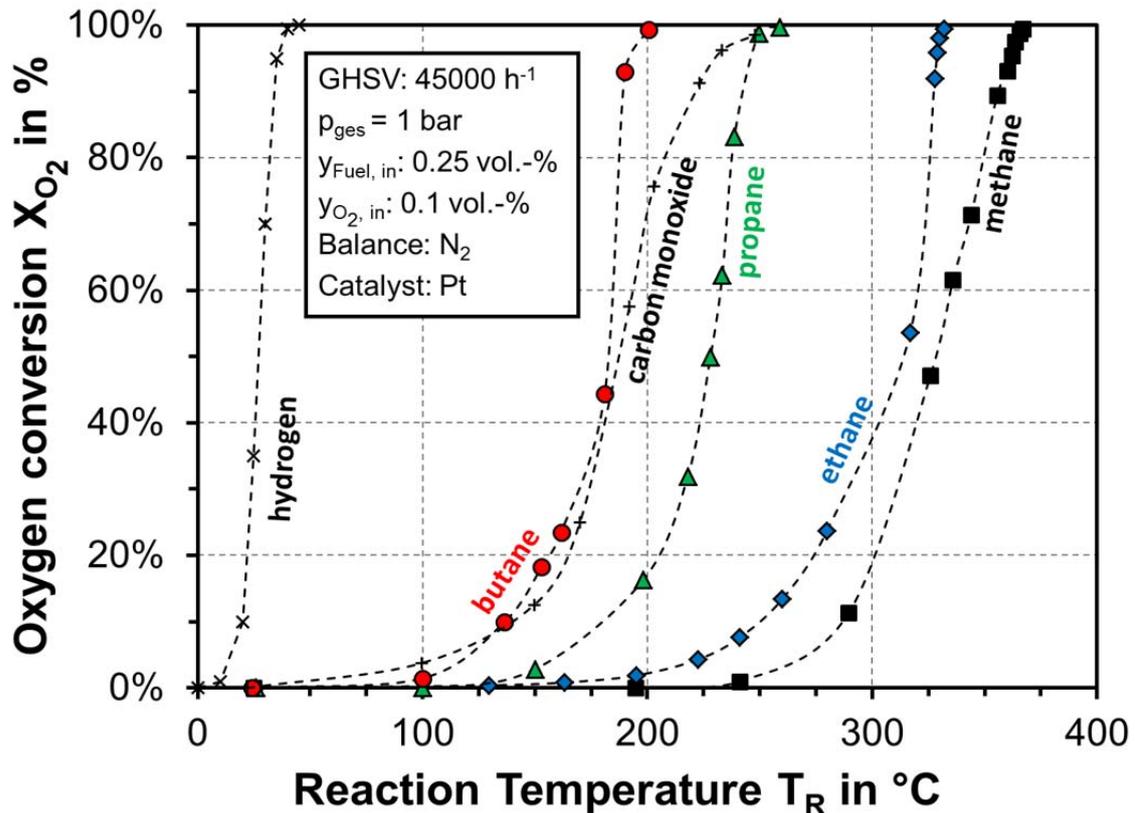
Fig. 5: Comparison of the activity of different fuel gases for the conversion of oxygen

As can be seen, methane exhibits the highest stability. Therefor the highest reaction temperature is necessary for methane conversion. Hydrocarbons follow the sequence: ethane > propane > butane. Carbon monoxide lies between propane and butane. Hydrogen features the highest reactivity and allows a complete conversion of 1.000 ppmv of oxygen at about 50 °C in the given experimental setup.

Comparison of Fig. 4 and Fig. 5 shows, that the temperature for complete conversion of 1.000 ppmv oxygen in methane equals the required temperature, when 0.25 vol.-% propane (or LPG) are applied for this task. This is due to the significant differences in partial pressures of the fuel gases, as the LPG content needs to be adapted to the amount of oxygen, while methane is available in large surplus in-situ in the gas stream.

Furthermore, Fig. 6 shows a comparison of different catalyst materials. While noble metals like platinum or palladium feature a high catalytic activity, transition metals like copper or nickel require higher reaction temperatures for complete conversion of oxygen. However, these materials exhibit economic benefits and therefore may also be applied for this task. In future, the focus of the ongoing work on catalyst optimization will be identifying an optimum between costs, performance and durability in respect to the critical minor constituents in biogas.
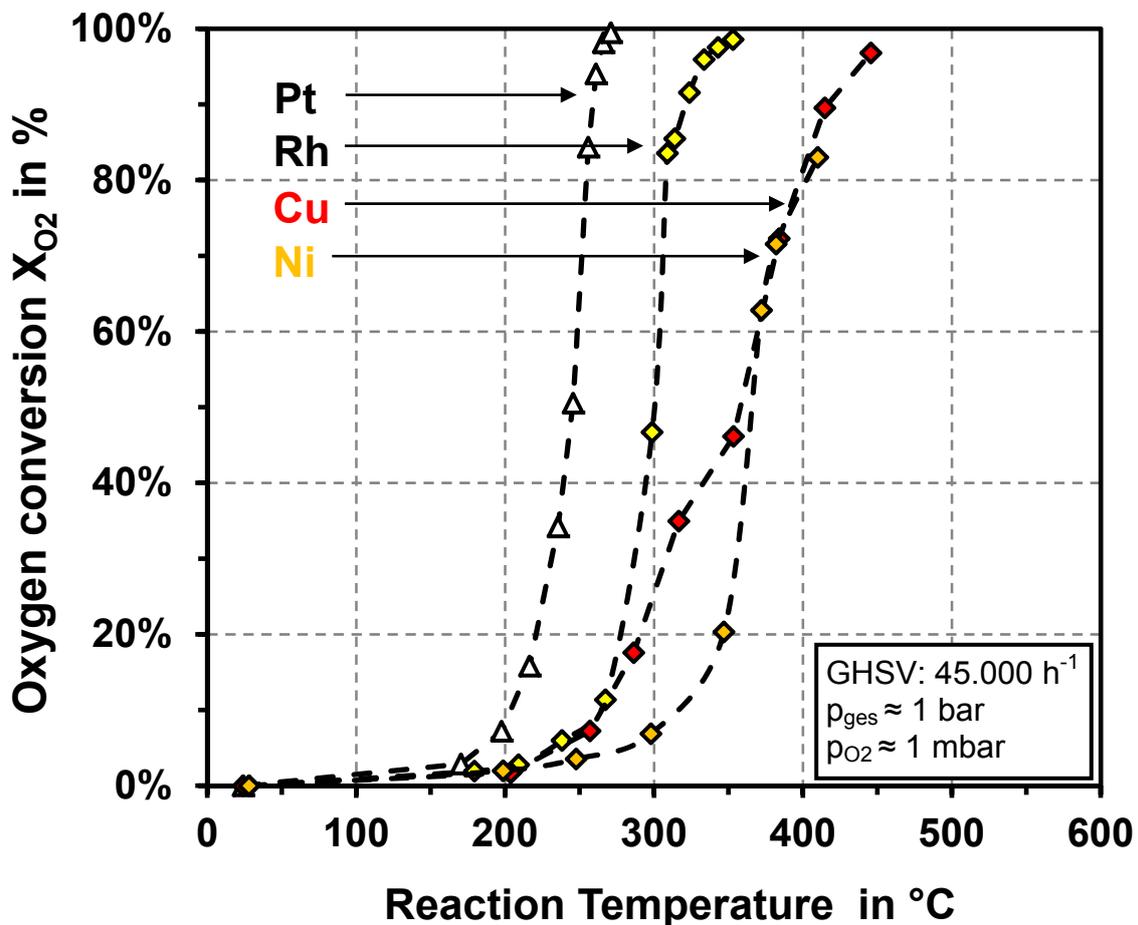
Fig. 6: Comparison of different catalysts for the conversion of oxygen by oxidation of methane

Against this background, a demonstration of the process with actual biogas from an injection plant was undertaken with a noble metal catalyst. This catalyst performed well for a Time on stream, TOS of approximately 170 h under severe operating conditions. The feed gas contained sulfur (mainly H_2S), siloxanes and ammonia-contamination. During the measurements, approximately 2.500 - 3.000 ppmv of oxygen was removed from the biomethane stream, the threshold value of 10 ppmv oxygen was met and the catalyst showed no significant deactivation.

6. Economics of catalytic oxygen removal processes

For a technical implementation of catalytic oxygen removal processes, a setup as shown in Figure 7 is necessary. In this arrangement, oxygen rich gas enters a preheater, where the temperature is raised to the desired reaction temperature. The reaction is carried out in a catalytic fixed-bed configuration. Afterwards, the flue gas is used to preheat the feed gas stream. For start-up, an electrical heater is applied. In case the oxygen content in the feed gas stream allows for an autothermal operation

mode, the electrical heater can be by-passed. This general scheme is valid for basically all relevant fuel gases.
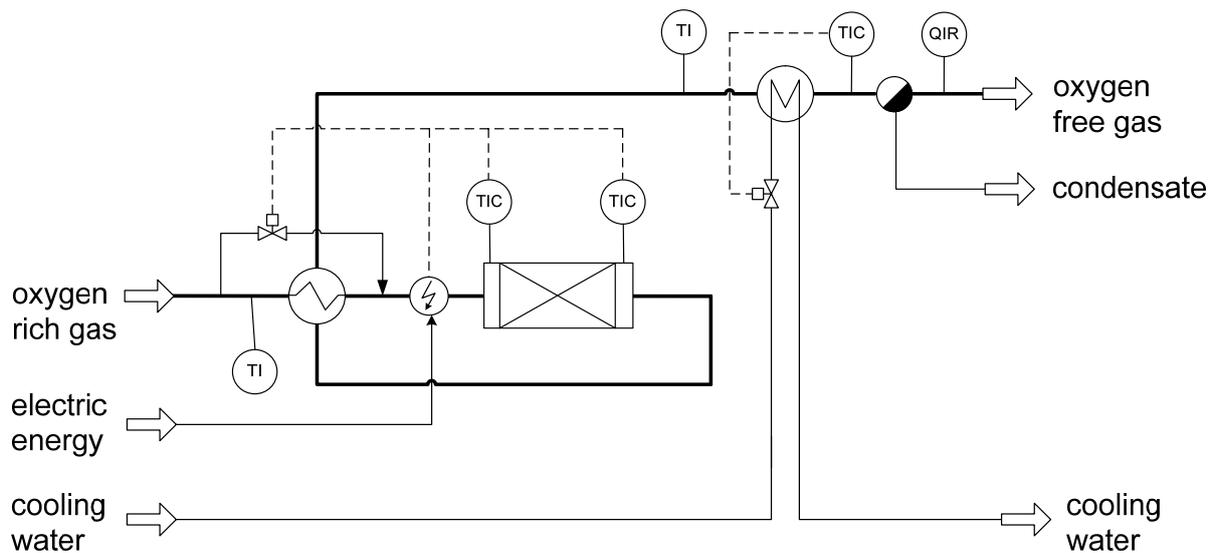
Fig. 7: General setup for oxygen removal by catalytic oxidation processes

Concerning the process economics in an autothermal operating mode, CAPEX is dominated by the required reaction temperature (which is directly linked to the scale of the economizer), while the expenses for the fuel gases are the major contribution to the operational costs. In the biogas case, all fuels, except methane, have to be supplied, stored on-site and added to the biogas stream separately. While the average price for biogas in Germany was at approximately 7 ct/kWh (H_S) in 2012 [17], hydrogen costs including an on-site hydrogen infrastructure range at approximately 25 - 30 ct/kWh (H_S). In the base-case of 0.5 vol.-% oxygen in biogas (biomethane capacity: 500 m³/h), an annual amount of at least 40.000 m³ hydrogen is necessary.

In this case, the use of hydrogen for oxygen removal results in specific costs of approximately 0.13 ct(EUR)/kWh (H_S) of biogas (CAPEX is included). For the same case, the catalytic oxidation of biomethane leads to economic benefits of approx. 20 – 40 %, despite CAPEX for methane more than doubles the hydrogen case.

Due to lower CAPEX, the maximum concentration for economically feasible implementation of hydrogen amounts to approximately 2.000 ppmv. When higher concentrations of oxygen are to be treated, e. g. in case physical scrubbers are used for CO_2-removal, methane should consequentially be used for oxygen removal instead.

7. Conclusions and perspectives

The application of methane as a reducing agent for oxygen is a promising alternative to state-of-the-art technologies for oxygen removal. For complete conversion of O_2 with methane, reaction temperatures of 250 - 350 °C are required, which is in the same range as required for application of propane for this purpose. An economic evaluation of the process shows, that, despite the higher CAPEX, the application of the methane oxidation leads to economic benefits, when oxygen concentrations exceed approximately 2.000 ppmv. Besides the fundamental examinations on process design, the process has been tested with technical biogas as a feed, including typical minor constituents of biogas. The experiments on-site confirmed the results with synthetic biogas mixtures, the catalyst showed reasonable performance concerning oxygen reduction and no deactivation.

Further on, experimental work on feed gas contamination with minor constituents will be continued for a better understanding of long-term effects on catalyst durability, as catalyst lifetime is as least as important as catalytic activity itself.

Acknowledgements

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