

# Direct Methanation of Flue Gas at a Lignite Power Plant

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**Abstract:** - The combustion of fossil fuels results in CO<sub>2</sub> emission, which is one of the primary causes of global warming. An important approach for solving this problem is the fixation, the chemical utilization and the recycling of CO<sub>2</sub>. Therefore, we investigate the catalytic conversion of CO<sub>2</sub> with H<sub>2</sub> into methane (CH<sub>4</sub>) with an upscaled test station at a brown coal power plant. In a completely new strategy, we realize the direct conversion of the CO<sub>2</sub> content of the flue gas, without a cleaning process like amine scrubbing or optimized combustion like oxyfuel. Our experiments are performed in matters of catalytic performance, heat production and stability of the catalytic Sabatier process, as a function of the gas flow rate. The catalytic performance is investigated with a simulated composition of flue gas and under real conditions directly at the power plant. The CH<sub>4</sub> production by the Sabatier process is realized with a maximum input flow rate of near 50Nm<sup>3</sup>/h, with 30Nm<sup>3</sup>/h flue gas and 20Nm<sup>3</sup>/h hydrogen. For these values, the necessary power scale for hydrogen generation by electrolysis is around 100kW. With synthetic and real flue gas, a conversion up to 99% (for hydrogen surplus) with 100% selectivity is stabilized. The reaction operates in thermal steady state equilibrium without any external energy supply. In consequence, the process of CO<sub>2</sub> recycling could be integrated directly as a post combustion process of conventional power plants, without an expensive capturing step, for example.

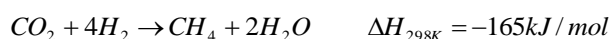
**Key-Words:** - CO<sub>2</sub> recycling, Power to Gas (PtG), Synthetic Natural Gas (SNG), Sabatier-Reaction, Flue Gas

## 1 Introduction

In the scope of the energy transition from fossil to renewable sources, we need new concepts for sustainable energy supply and energy storage, with a reduction of the greenhouse gas CO<sub>2</sub>. The conversion of CO<sub>2</sub> into methane, commonly known as methanation, is a promising approach for a CO<sub>2</sub> neutral production circle. In contrast to the concept of carbon capture and storage, methanation opens an opportunity for a reintegration and reuse of CO<sub>2</sub> in a recycling process in the form of synthetic natural gas (SNG).

The hydrogen for the hydrogenation must be renewable generated. In a “power-to-gas-to-power” approach (PtG), the hydrogen and methane stores energy with the possibility to use it in times of absence of regenerative power production. If methanation is integrated into plants for power- or cement-production for example, it could be an important contribution for an improvement of the industrial CO<sub>2</sub>- balance.

A conversion of CO<sub>2</sub> into CH<sub>4</sub> is possible by the Sabatier reaction



Although the methanation is thermodynamical favored, the reaction is limited in kinetics, and catalysts are required to achieve acceptable conversion from CO<sub>2</sub> into CH<sub>4</sub>. Common catalysts for the Sabatier reaction are based on nickel/nickel oxide on different substrates like Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, CaO or a combination of them [1,2].

Today in Germany, several plants for PtG-are in operation. For example, a PtG plant is installed 2016 in Rostock by Exytron GmbH. The plant is conceived as pilot plant for autarkic power supply, with a SNG production of 1Nm<sup>3</sup>/h. Another pilot plant with a SNG production of 60-220Nm<sup>3</sup>/h is the PtG plant in Allendorf. With an input power of 1100kW, SNG is produced from biogas for injection into the grid for natural gas. This plant is in operation since 2014. A further important example is a 250 kW plant for methanation, installed 2012 by the “Zentrum für Sonnenenergie und Wasserstoff-Forschung Baden-Württemberg (ZSW)” in cooperation with „Fraunhofer Institut für Windenergie und Energiesystemtechnik (IWES)“. The goal of the „Audi-e-gas“-project in Werlte is the production of SNG as fuel for a CO<sub>2</sub> free mobility. The project is started in 2011 and is

operated by the Audi AG. A review on PtG pilot projects in Germany is given in [3].

## 2 Problem Formulation

All above mentioned examples of methanation works with almost pure and clean CO<sub>2</sub>. If the emitted CO<sub>2</sub> of a lignite power plant is used as the “source” for such methane, a capturing step, respectively an upgrade of the burning process is necessary. The first strategy in this scope is a cleaning process like amine scrubbing [4], the second is the oxyfuel combustion, both resulting in almost pure CO<sub>2</sub> quality [5]. As a post combustion process, amine washing is promising, but like also the oxyfuel combustion, these steps require high investments. Therefore, research for possible alternatives is demanded.

This paper describes the Sabatier process for the direct conversion of flue gas emitted from a lignite coal power plant. In this context the meaning of the term „direct“ is that the flue gas is used without any separation/enrichment of CO<sub>2</sub>. The concept was investigated under real conditions at a power plant (1600MW).

The direct CO<sub>2</sub>-methanation from flue gas is scheduled as a post combustion approach: Even older power plants could be upgraded for methanation and cycling. A further process integration should be possible by using waste heat of the power plant for the catalytic reaction. Or as shown later, the heat production of the catalytic reactor is significant and could also be available for an improvement of the total process efficiency.

Of course, if the proof of principle for a direct methanation of flue gas without CO<sub>2</sub> enrichment is given, the possible field of applications for CO<sub>2</sub> methanation is enlarged: Not only the emissions of power plants could be recycled, but also the CO<sub>2</sub> content from flue gases of steel production, cement production or of refineries.

At laboratory scale with a reactor volume of 5cm<sup>3</sup>, we already investigated the Sabatier process in a simulated flue gas atmosphere [6, 7, 8]. The reaction was assessed with regards to conversion rates, yield, selectivity and long-term stability. Using a catalyst based on nickel, we extract a selectivity towards methane near 100% with a conversion of around 85%.

Also we examined the influence of oxygen and further typical contaminations like NO<sub>2</sub> and SO<sub>2</sub>. A content of around 5-6 vol-% oxygen is typical for flue gas. The catalytic performance for a variation of the oxygen content from 0 up to 8 vol% shows no changes in the catalytic activity, in principle. But the

efficiency of the process is lowered by the oxygen-hydrogen reaction. Here, the hydrogen, available for the Sabatier reaction is removed by this reaction, and the conversion and yield is lowered by the amount of lost hydrogen.

Sulphur is a critical contamination for the stability of Ni based catalysts. A concentration of around 70ppm (or 200mg SO<sub>2</sub>/m<sup>3</sup>) SO<sub>2</sub> is typical for flue gas [9]. Synthetic flue gas with a SO<sub>2</sub> contamination in such a concentration show a degradation of 1.36% in conversion per hour, but with a breakdown in performance after 40 hours, if a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> substrate is used [7, 8]. A further reduction of the SO<sub>2</sub> content is necessary for better long term stability. Nevertheless, the deactivation caused by SO<sub>2</sub> content is low in relation to a possible degradation caused even by traces of H<sub>2</sub>S.

## 3 Problem Solution

The experiments with an upscaled version are performed with the objective of a stable and acceptable conversion of CO<sub>2</sub>, with regard to the flow rate, the oxygen content in the flue gas, and the heat production. A further goal is an estimation of the heat production, compared to calculations, based on thermodynamic data.

To investigate these points, we build a test station, described here in section 3.1. In part 3.2, we introduce the basics for the characterization of the catalytic performance and describe the catalysts used in our experiments. Part 3.3 address the integration of our test station into the power plant.

The experiments described are separated into measurements with synthetic flue gas in the first part (3.4) and experiments with real flue gas directly at a power plant in the second part (3.5).

### 3.1 Setup of the test station

Table 1 gives the dimensions of the test station. The setup is mobile and is installed in a 40 feet ISO container. The flow rate is generally adjusted into the stoichiometric ratio of the Sabatier reaction with H<sub>2</sub>:CO<sub>2</sub> = 4:1. Also in the case of an O<sub>2</sub> additive for flue gas, this stoichiometric ratio is adjusted by a calculation of the hydrogen oxygen reaction, according to [7, 8]. The first line of table 1 gives the values for the total flow rate of the educt gas. If pure CO<sub>2</sub> is used, a total flow rate of 4H<sub>2</sub>+CO<sub>2</sub>=(20+5)Nm<sup>3</sup>/h is necessary. The value for the CO<sub>2</sub> flow rate per day is 120Nm<sup>3</sup>/day or 235kg CO<sub>2</sub>/day. With a yield of CH<sub>4</sub> in the range of 90%, this corresponds to a conversion of 212kg CO<sub>2</sub>/day

or  $108\text{Nm}^3 \text{CO}_2/\text{day}$ . For flue gas as the educt gas with a  $\text{CO}_2$  content of 15%, the resulting input flow rate is  $50 \text{Nm}^3 \text{H}_2/\text{h}$ . Here, the hydrogen is set as limiting factor for both, the pure  $\text{CO}_2$  and the flue gas, with a value of  $20\text{Nm}^3 \text{H}_2/\text{h}$ . This is shown in line two of table 1.

An energy of 4.5-5 kWh per  $\text{Nm}^3$  hydrogen is necessary, if alkaline water electrolysis is used [12]. Therefore, the power consumption for the generation of  $20\text{Nm}^3 \text{H}_2/\text{h}$  by electrolysis is 100kW for pure  $\text{CO}_2$  and for flue gas, ( line 3 of table 1).

	Pure $\text{CO}_2$	Flue gas with 15% $\text{CO}_2$
Total input flow / $\text{Nm}^3/\text{h}$	25	50
Demand of $\text{H}_2$ / $\text{Nm}^3/\text{h}$	20	20
Power for Electrolysis / kW	100	100
Converted $\text{CO}_2$ (at $X=90\%$ ) in $\text{Nm}^3/\text{h}$	4.5	4.0
Total output flow / $\text{Nm}^3/\text{h}$	7	30
Volume of reactor / liters	30	30
Mass of the catalyst / kg	25 (METH134)	25 (METH134)

Figure 1 shows the main components of the station. A more detailed description is given in [10,11]. Starting with the gas supply, the flow of the process gas is adjusted by mass flow controllers (MFC) for  $\text{CO}_2$  (maximal  $5\text{m}^3/\text{h}$ ),  $\text{H}_2$  (maximal  $20\text{m}^3/\text{h}$ ),  $\text{N}_2$  or flue gas (maximal  $50\text{m}^3/\text{h}$ ) and  $\text{O}_2$  (maximal  $3\text{m}^3/\text{h}$ ). MFC for  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{O}_2$  are necessary for measurements in synthetic flue gas. Hydrogen is delivered in conventional gas bottles during all experiments, flue gas is extracted directly from the emission stream of the power plant, after compression, described later in detail (part 3.3).

For starting the catalytic reaction, it is possible to preheat the process gas. We use commercial and flexible strip heaters with a maximal annealing temperature of  $900^\circ\text{C}$  for both, the preheating unit and the reactor. The strip heater is adapted to the reactor segment as a collar. This enables a stable operation even at temperatures around  $800^\circ\text{C}$ .

After preheating, the educt gas is guided into the reactor with an inlet pressure of 1-10bar, depending on the catalyst used. The reactor is designed as flow reactor and is build up by 10 segments in maximum, each with a volume of 3 liters (figure 2). Each segment is made by standard CF steel and fixed by a flange sealed by an oxygen free (OHCF)-copper ring. The segments are filled separately with the catalyst. For starting the Sabatier reaction, the preheating system and the reactor chambers are heated with the stripe heaters up to a temperature of  $350^\circ\text{C}$ . This temperature is necessary to reach high

Of course, due to the content of nitrogen of flue gas (around 80% with water, table 2), the total input/output flows for pure  $\text{CO}_2$  and flue gas are different. Due to the oxygen-hydrogen reaction, the amount of converted  $\text{CO}_2$  is lower for flue gas (line 4) (or in a reversed way: For the same amount of converted  $\text{CO}_2$  ( $4.5 \text{Nm}^3/\text{h}$ ), we need more hydrogen). The total mass of catalyst includes the amount of nickel oxide (25%) plus the substrate ( $\text{Al}_2\text{O}_3$ ).

enough reaction rates (of the Sabatier reaction) for the Ni-catalyst used [6, 11]. In the later stage of the exothermal Sabatier reaction, no heating of the reactor chamber is necessary.

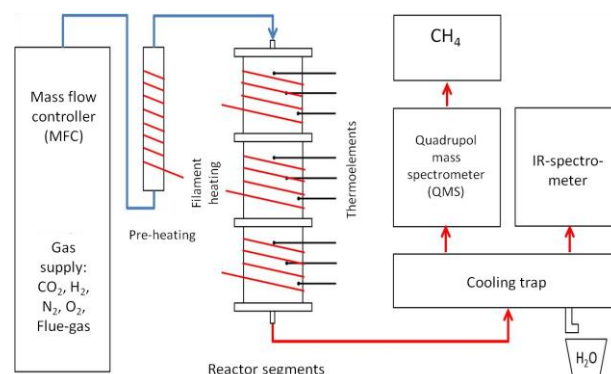
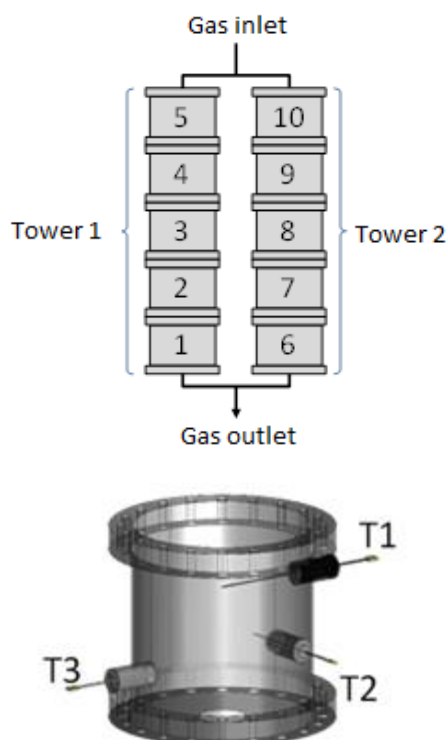


Fig. 1. Schematic of the test station for methanation

For better representation, each segment of the reactor unit is identified with a fixed number (figure 2). The temperature of each segment is measured with three thermocouples at different positions inside the reactor chamber (figure 2). For clarity of presentation, we define the average temperature for each segment, as

$$\bar{T} = (T_1 + T_2 + T_3) / 3 \quad (1)$$



**Fig. 2.** Top the reactor, in modular setup with ten segments, each with a volume of 3 liters, with numbering for better representation. Down: One segment of the reactor with placing of thermocouples

The thermocouple T3 (figure 2) is used for the thermal management of the reactor: Below a temperature of 350°C, the heating system is switched on, above this, the reaction runs without heating.

After reaction, the product gas is guided into a cooling trap for condensation of water, produced during the Sabatier reaction (figure 1). The mass of condensed water gives a coarse estimation of CO<sub>2</sub> conversion. Also a reduced amount of water is necessary for a stable analysis of the gas composition. The gas analysis is connected via a bypass for only a part of the main product gas. As analytical system, we use two independent methods with the opportunity for a cross check of the reaction: first gas sensors for CO<sub>2</sub>, CH<sub>4</sub> and CO (infrared) and H<sub>2</sub> (thermal conductivity), and second a quadrupole mass spectrometer. The UHV system of the mass spectrometer is connected to the product gas stream with a typical pressure of 1-10bar by a pinhole of 6µm in diameter. An amount of the product gas stream flows into the vacuum chamber for analysis, with a time delay of around one minute. With such a setup, a connection of

atmospheric pressure and ultra high vacuum with an analysis of the ad- and desorption of CO<sub>2</sub> by thermal desorption spectroscopy (TDS) is possible [13]. The maximum of detectable mass is 100amu for our device, a screening of byproducts is possible in this range.

All devices are controlled by LabView. In addition to the monitoring of the reactor line, the following data are recorded: Temperature versus time, gas concentration and input gas flow.

### 3.2 Catalysis

The catalytic performance is calculated as follows: According to standard definition [14] of parameters for the catalytic performance, we calculate for the CO<sub>2</sub> conversion  $X_{CO_2}$

$$X_{CO_2} = \frac{\dot{n}_{CO_2,in} - \dot{n}_{CO_2,out}}{\dot{n}_{CO_2,in}} \quad (2)$$

for the CH<sub>4</sub> yield  $Y_{CH_4}$

$$Y_{CH_4} = \frac{\dot{n}_{CH_4,out}}{\dot{n}_{CO_2,in}} \quad (3)$$

and for the selectivity  $S_{CH_4}$

$$S_{CO_2}^{CH_4} = \frac{Y_{CH_4}}{X_{CO_2}} = \frac{\dot{n}_{CH_4,out}}{\dot{n}_{CO_2,in} - \dot{n}_{CO_2,out}} \quad (4)$$

Here, “ $\dot{n}$ ” is the amount of substance per unit of time, either as educt (“in”) or as product (“out”). For a selectivity of  $S=1$ , the calculation of the CO<sub>2</sub> conversion  $X_{CO_2}$  is possible directly by an analysis of the outgoing product gas stream, here:

$$X_{CO_2} = \frac{\dot{n}_{CH_4,out}}{\dot{n}_{CH_4,out} + \dot{n}_{CO_2,out}} \quad (5)$$

For the mass spectrometer system, the CH<sub>4</sub> and CO<sub>2</sub> concentrations in the product gas are calculated from the intensities for the related mass numbers, according to

$$\begin{aligned} c_{CH_4,out}^{MS} &\sim \gamma_{CH_4} I_{CH_3^+}^{MS} \\ c_{CO_2,out}^{MS} &\sim \gamma_{CO_2} I_{CO_2^+}^{MS} \end{aligned} \quad (6)$$

The concentration of CH<sub>4</sub> (16amu) is calculated from the CH<sup>3+</sup> (15amu) intensity, due to superposition of the 16amu signal with an oxygen residual in the vacuum chamber (H<sub>2</sub>O and O<sub>2</sub>). The

concentration of CO<sub>2</sub> (44amu) is directly measured from the 44amu signal. The proportionality constants  $\gamma$  includes the characteristic ionization cross section, the fragmentation probability and a calibration factor of our setup ( $\gamma=0.5$  for CH<sub>4</sub>;  $\gamma=0.29$  for CO<sub>2</sub> [15]). In our measurements with the mass spectrometer, we assume a selectivity of S=1 (this in good approximation, using our own results in laboratory scale [6, 11]) and use equation (5) for CO<sub>2</sub> conversion.

For ease of evaluation, scaling and comparison, we need the normalized input flow, defined as the gas hourly space velocity (GHSV) [16]

$$GHSV = \dot{V}_{in} / V_{Reactor} \quad [\text{h}^{-1}] \quad (7)$$

with  $\dot{V}_{in}$  as input flow in Nm<sup>3</sup>/h and  $V_{Reactor}$  as total reactor volume (or the total volume of the catalyst, here our fixed-bed). In our setup, the maximum GHSV is therefore 830h<sup>-1</sup> for working with pure CO<sub>2</sub>. This value is duplicated to around 1660h<sup>-1</sup> for flue gas. For ten segments this is equivalent to an overall input flow rate of 25Nm<sup>3</sup>/h with pure CO<sub>2</sub> (and H<sub>2</sub>) and 50Nm<sup>3</sup>/h for flue gas (and H<sub>2</sub>). When reducing the number of segments, we reduce the flow rate proportionally while keeping a constant GHSV.

Usually, the GHSV is used to describe the technical value for the mass flow and is not sufficient for a direct analysis and comparison of the catalytic activity. For this purpose, the true velocity or equivalently the bed residence time of a molecule inside the fixed bed of the catalyst is necessary. The mean migration time of the gas molecule is determined by the open volume between the grains or spheres of the reactor bed. For the comparison of the catalytic activity, we use the mean bed residence time as

$$t_{Residence}^{Bed} = V_{Open} / \dot{V}_{in} \quad [\text{s}] \quad (8)$$

with  $V_{Open}$  as open volume between the grains or spheres of the catalyst.

The Sabatier reaction with real flue gas is performed in a fixed-bed reactor with two different catalysts, both on Ni basis. A good performance of such catalysts is confirmed by our experiments in laboratory scale with a 5cm<sup>3</sup> reactor (see introduction and [11]).

As first catalyst, we use nickel, supported on a combined silica/alumina substrate with a content of 65wt% Ni (Sigma Aldrich, no. 208779) and an active surface of 190m<sup>2</sup>/g BET. In a 40 day run at

laboratory scale, this catalyst show 95% conversion and a selectivity of 100%, at 350°C [11]. To prevent hot spots and related sintering effects, we distribute the Ni-based catalyst powder in a bed of quartz sand with a grain size of 0.5 up to 1mm.

Tests of CO<sub>2</sub> conversion versus content of catalyst in quartz sand shows a saturation in conversion at 50-100g pure nickel per segment, with a CH<sub>4</sub> selectivity of 100% for low flows/GHSV, here 208h<sup>-1</sup>. So we use 105g catalyst or 68g pure Ni per segment in the fixed-bed of quartz sand for all further experiments and especially at the power plant. In total, 4kg of the active blend (catalyst plus quartz sand bed) is used for each segment. The resulting Ni-concentration is only 1.7% in each segment.

An estimation of the relative open volume (porosity) is possible by a comparison of the densities of the reactor bed ( $\rho_{SiO_2-Sand}$ ) with the theoretical density of quartz ( $\rho_{SiO_2}=2.65\text{g/cm}^3$ ). The relative open volume of the catalytic blend is given as  $V_{open} / V_{total} = 1 - \rho_{SiO_2-Sand} / \rho_{SiO_2}$ . The relative open volume (porosity) of our active blend is 40%. To maintain the flow rates of product gas given in table 1, a high pressure drop from 8-10bar at the input of the reactor down to 1bar at the output is necessary for such a fixed-bed reactor.

For another commercially available nickel based catalyst, a granulated material in the form of spheres with 3-6mm in diameter, such a high pressure drop along the reactor is not necessary, the difference in pressure is in a range of 1bar. The catalyst is distributed as "METH134" C&CS, Zorneding, with a NiO content of 20 up to 25% on Al<sub>2</sub>O<sub>3</sub> substrate. For this catalyst, an additional bed of catalytic inactive spheres (like quartz sand) was not necessary. The relative open volume between the spheres is approximately 54%, measured by the weight of additional water to fill the open volume between the (water-saturated) spheres.

### 3.3 Integration of the test station into the power plant

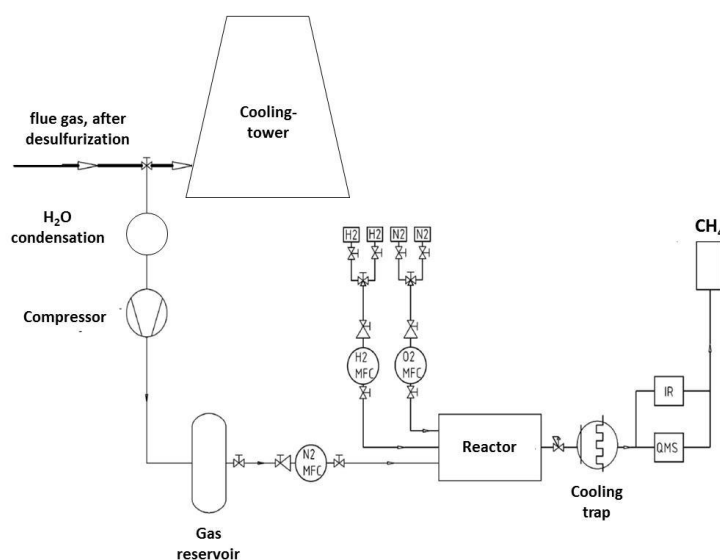
The lignite power plant was selected for our experiments with flue gas, because the SO<sub>2</sub> content of this power plant is below 200mg SO<sub>2</sub>/m<sup>3</sup> (or 70ppm) after flue gas desulfurization. As mentioned in the introduction part, a small, but acceptable drift of 1.36% in conversion per hour is measured for our catalysts.

The flow sheet of the integration of our mobile test station into the power plant is shown in figure 3. Flue gas from the power plant is used after

desulfurisation. For this purpose, a small part of the main gas stream is extracted with a pipe reaching 2m inside the flue gas channel of the power plant. Inside the flue gas channel, the gas has a temperature of 68°C and is water saturated. By using a compressor, a gas flow from the flue gas channel of the power plant to our methanation station is realised. During the flow over a distance of 40m, the flue gas is cooled down to room temperature. Therefore, a trap for the condensed water is installed in front of the compressor. By condensation, most of the water together with the

SO<sub>2</sub> content as sulfuric acid is separated from the educt gas. After the compressor, the flue gas is stored with a pressure of up to 10bar inside a buffer storage to ensure a stable gas flow. For methanation, the gas is guided via metallic tubes to the gas mixing unit of our container. The flow is controlled by an MFC for N<sub>2</sub>.

During the measurements with synthetic and real flue gas we record our data under the following criteria: Temperature, CO<sub>2</sub>-conversion, CH<sub>4</sub>-yield and quantity of converted CO<sub>2</sub> as functions gas flow and of time.



**Fig. 3.** Schematic of the integration of the setup for methanation into the 1600MW power plant. The flue gas from the main gas stream has to be guided via a compressor to the methanation reactor. MFC: Mass-flow-controller, IR: Infrared gas sensors, QMS: Quadrupole mass spectrometer.

### 3.4 Experiments with pure CO<sub>2</sub> and synthetic flue gas

Before the measurements with real flue gas at the power plant are started, we perform a series of tests with pure CO<sub>2</sub> and synthetic flue gas. The synthetic flue gas is mixed from pure gases from compressed gas containers. We adjust the amount of these gases according to the composition of flue gas for a conventional power plant in operation.

After flue gas desulfurization (FGD) and flue gas condensation (FGC), the composition is given in table 2. The typical ratio of N<sub>2</sub>/CO<sub>2</sub> is around five, with a residual amount of O<sub>2</sub>, in the range of 6Vol% in flue gas. This is a relatively high value, mainly due to an extra addition of oxygen for an optimized combustion. As already revealed in experiments in laboratory scale, the high exothermic hydrogen-oxygen reaction



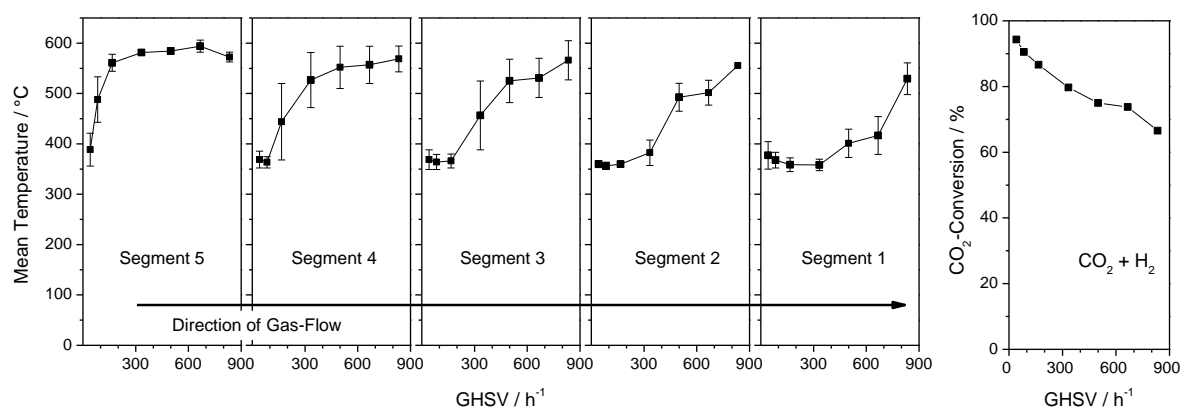
plays an important role for the Sabatier reaction with oxygen contaminations [7, 8]. Therefore, experiments under controlled conditions with stepwise addition of oxygen are necessary.

N <sub>2</sub> +H <sub>2</sub> O Vol%	CO <sub>2</sub> Vol%	O <sub>2</sub> Vol%	SO <sub>2</sub> ppm	NO <sub>2</sub> ppm
78.5	15.5	6	63	46

In a first series of experiments, beside other dependencies (pressure, number of segments [10, 11]), we investigate the influence of the input flow rate on the catalytic performance for pure CO<sub>2</sub>. This is important as reference. Therefore, we plot the temperature  $\bar{T}$ , defined in equation (1) and the CO<sub>2</sub> conversion versus GHSV. As expected, the conversion drops down for higher flows inside the reactor. Mass flow increases with higher flow rates and consequently, the heat production per time or

the temperature increases. A gradient in temperatures from segment to segment is also visible, indicating a fast reaction just at the gas input in segment 5. For higher flows, temperatures are

homogeneous with an equilibrium at around 600°C. The pressure drop during the experiment is 8bar from gas input to gas outlet, for all flows.



**Fig. 4.** Pure CO<sub>2</sub>: Temperature  $\bar{T}$ , defined in (1) and CO<sub>2</sub> conversion, defined in equation (5) versus GHSV. Catalyst used: Ni/NiO, supported on a combined silica/alumina substrate as blend in quartz grains. Five segments are used. A GHSV of 830h<sup>-1</sup> represents the maximum input flow of total 25Nm<sup>3</sup>/h (20Nm<sup>3</sup>/h of H<sub>2</sub> and 5Nm<sup>3</sup>/h of CO<sub>2</sub>).

In a next step, we investigate the performance in synthetic flue gas with a representative composition of five parts N<sub>2</sub>, four parts H<sub>2</sub>, one part CO<sub>2</sub>, and stepwise increased amounts of oxygen. The performance is characterized without SO<sub>2</sub> and NO<sub>2</sub> contaminations.

The results are summarized in figure 5A, B. In Figure 5A, we plot the mean temperature, defined in equation (1) and in figure 5B the CO<sub>2</sub> conversion according to equation (5), both versus the percentage of oxygen in the flue gas, this for one segment and with a GHSV of 1600h<sup>-1</sup> to 1800h<sup>-1</sup>. These differences in GHSV are due to the variation in oxygen content. The input pressure during the experiments is 8bar (output 1bar). The catalyst used is Ni, supported on a combined silica/alumina substrate as blend in quartz grains.

In figure 5A, the grey area between 350°C and 550°C indicates the temperature range, which ensure high reaction rates near thermodynamical equilibrium (350°C) and high selectivity for methan, without side reactions (e.g. reversed water gas shift towards CO). The validity of this temperature range is revealed by experiments in laboratory scale [11].

Without any oxygen, the temperature of the reactor is outside the gray area. This low reactor temperature is due to a cooling effect of the inert N<sub>2</sub> component. The mean temperature  $\bar{T}$  is only 140°C for synthetic flue gas without any oxygen. For flue gas, the CO<sub>2</sub> component is thinned out by a factor of around five in respect to pure CO<sub>2</sub>. Therefore, the density of exothermal energy production by the

Sabatier reaction should be changed by a factor of 0.2 for same flow. Prerequisite for such a heat production would be an unchanged kinetics of the Sabatier reaction, but this is of course not the case. The temperature of 140°C is a result of our external heating with stripe heaters wrapped around the reactor segment. For a significant conversion with heat production, this (external) temperature is too low.

By introducing stepwise oxygen into the system, temperature starts to increase, linear from 140°C without oxygen up to 700°C for 10% oxygen. Just in the relevant oxygen content of 4-6%, the temperature is optimal for a stable and fast kinetics of the Sabatier reaction, in a range of 350°-550°C. Of course, this additional heat production is due to the reaction of the oxygen with hydrogen. This reaction is also responsible for a decreased conversion of CO<sub>2</sub>, this is clearly demonstrated for experiments in laboratory scale [7, 8]: Hydrogen for the Sabatier reaction is consumed by the reaction with oxygen and the conversion of CO<sub>2</sub> or the yield of CH<sub>4</sub> is simply proportional to this decrease.

This aspect is also visible in figure 5B for the CO<sub>2</sub>-conversion plotted versus oxygen content. The conversion first drops down and for the third data point, it starts to grow with increasing temperature and with a maximum in a range of 4-6% oxygen content. The reason for the dropdown in conversion for low oxygen content (1%) is obviously the oxygen-hydrogen reaction with a consumption of the hydrogen.

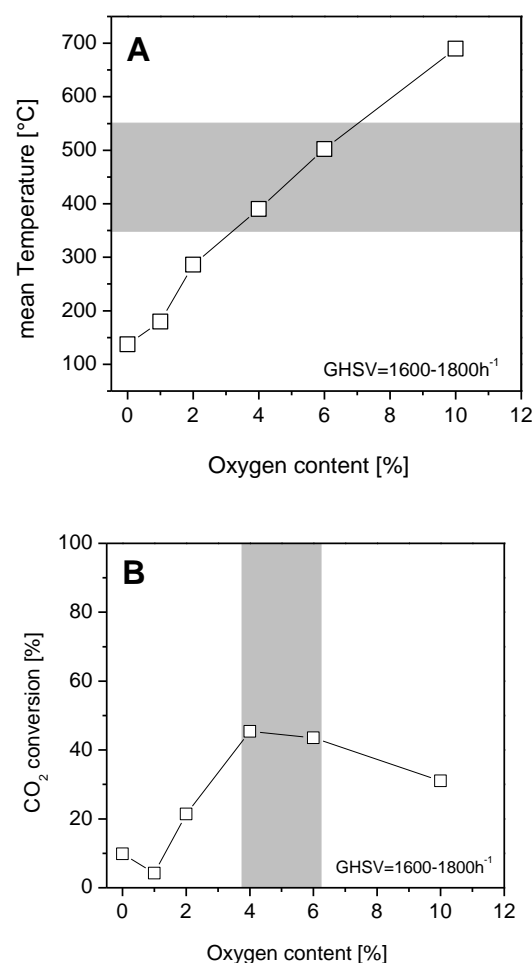
The relevant scale for the oxygen content of flue gas of lignite power plants is shown in figure 5B as gray area. For 6% oxygen, we have a temperature of 500°C with a conversion of 43.5%. The calculated conversion for the Sabatier reaction in thermodynamical equilibrium is 66.5% for 500°C at a pressure of 1bar [11, 17]). So the measured value for the conversion of CO<sub>2</sub> is low with respect to the thermal equilibrium at our P-T conditions. This has two main reasons: The first reason is the consumption of hydrogen based on the oxygen-hydrogen reaction, and the second reason is the very high flow rate, respectively the low residence time of the reactants inside the reactor. As confirmed by measurements in laboratory scale, the effect of hydrogen consumption on the CO<sub>2</sub> conversion is expressed by  $X_{CO_2}(P_{O_2}) = X_{CO_2}^0 (1 - 3P_{O_2} / (1 - P_{O_2}))$  with P<sub>O<sub>2</sub></sub> as content of oxygen in Vol-% and X<sup>0</sup> as CO<sub>2</sub> conversion without oxygen (equation is derived for a ratio of N<sub>2</sub>:CO<sub>2</sub>=5:1 in [7]). For the data point with 6% oxygen in figure 5B, we measure a conversion of 43.5%. If we take above equation, insert  $X_{CO_2}(P_{O_2}) = 43.5\%$  and  $P_{O_2} = 6\%$ , than X<sup>0</sup>, the conversion without oxygen, should be in the range of 54%. This value is below the conversion in thermodynamical equilibrium (66.5%). Therefore, an additional effect of residence time plays a role.

It is notable that the highest conversions are reached for oxygen concentrations normally found in flue gas. More important is the fact, that at this oxygen content and flow rate no external heating is necessary. In contrary, to ensure high conversion rates, the reactor should be cooled down for high efficiencies. The exothermic energy of the reaction is available for further integration into the process (e.g. preheating of inlet gas, high temperature electrolysis).

In conclusion, if flue gas with a content of 4-6% oxygen is used for a direct methanation of the CO<sub>2</sub> component, the resulting exothermic heat production is sufficient for a stand-alone Sabatier reaction without external annealing.

On one hand, the exothermic energy of the hydrogen-oxygen reaction is a prerequisite for direct methanation of flue gas, on the other hand hydrogen is consumed by this reaction and lowers the conversion of CO<sub>2</sub>.

To ensure an optimal CO<sub>2</sub>-conversion during our experiments at the power plant, we stabilize the stoichiometric ratio of H<sub>2</sub>:CO<sub>2</sub>=4:1 for the Sabatier reaction by adding an additional amount of hydrogen with respect to the measured oxygen content of the flue gas.



**Fig. 5.** Synthetic flue gas: (A) Temperature  $\bar{T}$ , defined in (1) and (B) CO<sub>2</sub> conversion, defined in equation (5) versus the content of oxygen in the input gas stream. Catalyst used: nickel, supported on a combined silica/alumina substrate as blend in quartz grains. The experiments are performed with one segment. The GHSV is 1600 h<sup>-1</sup> up to 1800 h<sup>-1</sup>. In (A), the grey area between 350°C and 550° marks the stable region for the Sabatier reaction without side products, as revealed by experiments in laboratory scale [6, 10, 11]. In (B), the grey area between 4 and 6% indicates the typical oxygen content of flue gas, according to table 2.

Figure 6 shows the influence of the kind of catalyst used, measured in synthetic flue gas with hydrogen compensation. A difference of around 10% in conversion is obvious for silica-alumina blend in quartz grains and the second catalyst Meth134, if the conversion is plotted versus GHSV, figure 6A. With equation (7), GHSV is just a normalized input volume flow. A more accurate comparison is given by plotting the CO<sub>2</sub> conversion versus the bed residence time, as described in equation (8). This is shown in Figure 6B. Here, no



significant differences between the two catalysts are visible.

The reason for the difference of 10% in figure 6A is the residence time at the same input flow/GHSV. For nickel, supported on a combined silica/alumina substrate as blend in quartz grains, an open space of 40% was found. In contrast, for nickel on alumina substrate as spheres (METH134), we found a relative open volume of 54%. Therefore, for same input flow/GHSV, the residence time for a molecule inside the reactor is higher by a factor of  $54/40=1.35$ . In consequence, a higher conversion at same total mass flow is possible for this catalyst, just due to a higher open volume. As revealed by the residence time, the catalytic activity is nearly the same for both catalysts.

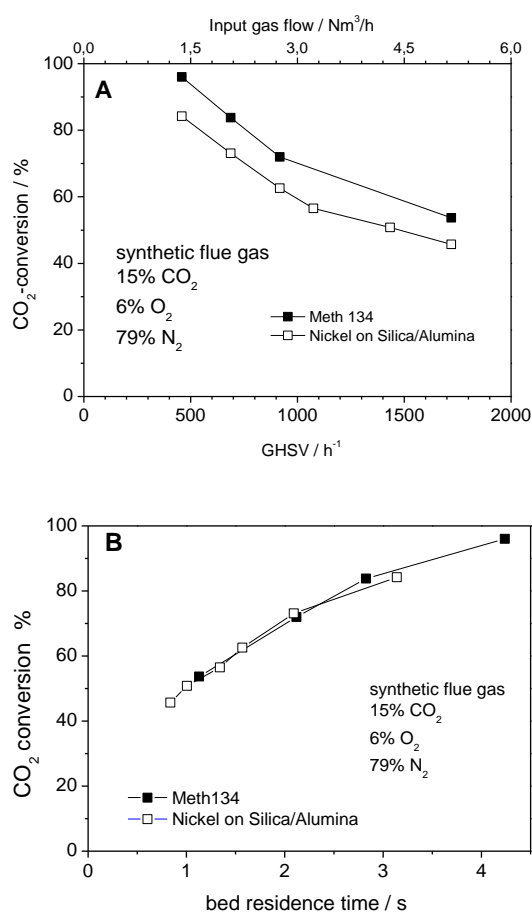
### 3.5 Experiments with real flue gas of a lignite power plant

The first experiments at the power plant are measurements of  $\text{CO}_2$  conversion versus temperature over time, for a constant gas flow (GHSV). We used 5 segments here. The content of  $\text{O}_2$  and  $\text{CO}_2$  in the flue gas was 6% and 13%, measured by mass spectrometer. At a GHSV of  $1667\text{h}^{-1}$ , a maximum in conversion and yield was found at a value of 80% for both, but with a decrease down to 60% in conversion and 50% in yield after 80 minutes with constant gas flow. During 80 minutes, a temperature gradient inside segment 5-4 is equilibrated into around  $580^\circ\text{C}$ , the temperature of segment 1 is constant at  $400^\circ\text{C}$ . The mean temperature is higher after 80 minutes and causes a shift of thermodynamical equilibrium of the Sabatier reaction with lower conversions [10, 11].

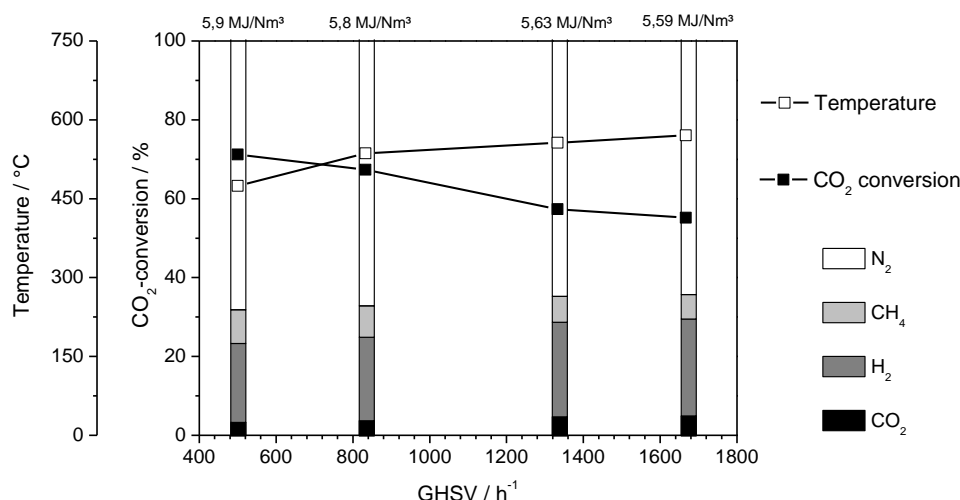
A further important part is the measurement of the influence of mass flow. For a GHSV from a value of  $500\text{h}^{-1}$  up to  $1660\text{h}^{-1}$ , a gradient in temperatures from segment to segment is again measured. For a flow of  $500\text{h}^{-1}$ , the temperature starts at  $550^\circ\text{C}$  in segment 5 (the gas input) and drops down to  $400^\circ\text{C}$  in segment 1 (the gas output). For a flow of  $1670\text{h}^{-1}$ , the temperature starts again at  $550^\circ\text{C}$  in segment 5 and remains almost constant over all 5 segments.

In figure 7 the  $\text{CO}_2$  conversion and the mean temperature for all five segments versus GHSV is given. Also the composition of the product gas with the resulting gross caloric value in  $\text{MJ}/\text{Nm}^3$  is shown. The  $\text{CO}_2$  conversion drops from 71% for the lowest GHSV down to 55% for the maximum

GHSV of  $1660\text{h}^{-1}$ . As a consequence, the remaining  $\text{CO}_2$  content increases slowly, as visualized in the gas composition. If the mass flow is higher (a factor of 3.34), the heat production due to the exothermic Sabatier and the oxygen hydrogen reaction is increased and enlarges the mean temperature of the reactor. This higher temperature causes a shift of thermodynamic equilibrium towards lower  $\text{CO}_2$  conversions. Due to smaller conversions, the gross caloric value decreases slightly from  $5.9\text{MJ}/\text{Nm}^3$  for  $500\text{h}^{-1}$  to  $5.6\text{MJ}/\text{Nm}^3$  for  $1660\text{h}^{-1}$ . With a mean gross caloric value of  $5.74\text{MJ}/\text{Nm}^3$  the product gas can be described as so called lean gas. This low value is of course due to the high content of inert gas



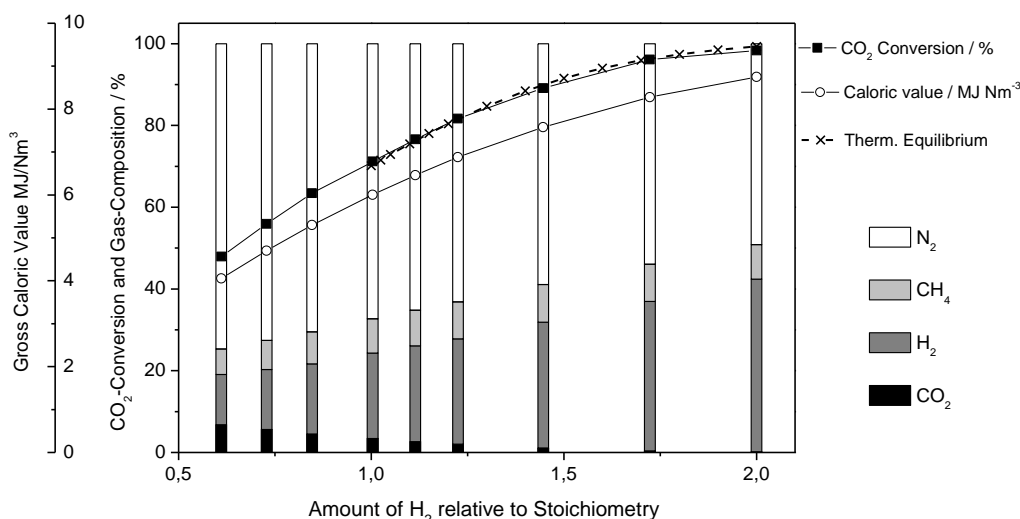
**Fig. 6.** Synthetic flue gas: (A), conversion of  $\text{CO}_2$  as function of GHSV, eq. (7), and (B), bed residence time, eq. (8) for the two catalysts used at the power plant. Experiments were performed with  $\text{H}_2$ -compensation (see text) for one reactor segment with 3 liters in volume.



**Fig.7.** Real flue gas. The CO<sub>2</sub> conversion and the mean temperature for all five segments is plotted versus GHSV. Also the composition of the product gas (stacked bars) with the gross caloric value in MJ/Nm<sup>3</sup> is given. We use Ni/silica-alumina blend in quartz grains as the catalyst.

From thermodynamics, a further increase of conversion is expected for a relative surplus of hydrogen. Figure 8 gives a summary of these measurements. The plot shows the product gas composition, conversion and gross caloric value in MJ/Nm<sup>3</sup>, versus hydrogen content of the educt gas, related to the stoichiometric ratio of H<sub>2</sub>/CO<sub>2</sub> = 4/1.

The GHSV is between 730 h<sup>-1</sup> and 1120 h<sup>-1</sup>. For H<sub>2</sub>/CO<sub>2</sub> ≤ 4/1, we use METH134, for H<sub>2</sub>/CO<sub>2</sub> ≥ 4/1, we use Ni/silica-alumina blend in quartz grains as the catalyst. A clear positive effect of hydrogen surplus is visible for H<sub>2</sub>/CO<sub>2</sub> ≥ 4/1. For a hydrogen surplus of “2”, this is H<sub>2</sub>/CO<sub>2</sub> = 8/1, the CO<sub>2</sub> conversion is 99% and no residual CO<sub>2</sub> is measured.



**Fig. 8.** Real flue gas. CO<sub>2</sub>-conversion, product gas composition (stacked bars) and gross caloric value in MJ/Nm<sup>3</sup>, versus hydrogen content of the educt gas, related to the stoichiometric ratio of H<sub>2</sub>/CO<sub>2</sub> = 4/1 after oxygen compensation. An amount of H<sub>2</sub> with “1” represents stoichiometry. The GHSV is between 410-and 480 h<sup>-1</sup>. For H<sub>2</sub> ≤ “1”, we use METH134 as catalyst, for H<sub>2</sub> ≥ “1”, we use Ni/silica-alumina blend in quartz grains as the catalyst. In addition, a curve for the thermodynamical equilibrium for the conversion is shown (dashed line).

Due to the surplus of hydrogen, the caloric value of the product gas increases. The gross caloric value starts from 4.0MJ/Nm<sup>3</sup> for a ratio of “0.6” or

H<sub>2</sub>/CO<sub>2</sub> = 2.4/1 and ends at 8.75MJ/Nm<sup>3</sup> for a ratio “2” or H<sub>2</sub>/CO<sub>2</sub> = 8/1.

The increased conversion is indeed a result of a shift in thermodynamical equilibrium towards higher conversions [10, 17]. In Figure 8, we also show the calculated curve for the thermodynamical equilibrium in conversion (dashed line). The calculation of the thermodynamical equilibrium is done by minimization of the Gibbs free energy for the Sabatier reaction without side reactions. The thermodynamical data for heat capacity, standard enthalpy and entropy with respect to temperature are from the NIST web site [18].

During our measurements at the power plant we realized a maximum input gas-flow of 27 Nm<sup>3</sup>/h flue gas. With all 10 segments, such a flow corresponds to a GHSV of 1494h<sup>-1</sup>, respectively a CO<sub>2</sub>-conversion of around 150kg/day, if a CO<sub>2</sub> concentration of 13% and a conversion of 90% in the flue gas is assumed. Without any external temperature management, the reaction is a stand-alone system due to own heat production. The temperature over all segments is equilibrated at 550°C for this gas-flow. The conversion of CO<sub>2</sub> is constant at a value of 64%, started from 90% for a GHSV of 415h<sup>-1</sup>.

A degeneration of the catalyst due to sintering at high temperatures or remaining traces of sulfur (as SO<sub>2</sub>) is not observed. One reason is our experimental setup: the water saturated gas flow from the power plant with 68°C cools down to room temperature along the way to the compressor system. This water is collected in a trap and the SO<sub>2</sub> content is solved as sulfuric acid in this condensated water. The result is a reduced SO<sub>2</sub> content in the input gas with a much lower degeneration of the catalysts as expected from experiments on laboratory scale. Another reason is the short possible time scale of our measurements without a notable reduction in catalytic activity.

For 30Nm<sup>3</sup>/h flue gas with a composition given in table 2, a possible power production of 22.26kW is calculated thermodynamical for 100% conversion of the Sabatier reaction and the oxygen-hydrogen reaction [11]. According to the composition in table 2, we calculate a total demand of 22Nm<sup>3</sup>/h hydrogen for the compensation of oxygen and for a stoichiometric ratio of H<sub>2</sub>:CO<sub>2</sub>=4 of the Sabatier reaction. The resulting power for hydrogen production by electrolysis with an energy demand of 5kWh/Nm<sup>3</sup> hydrogen is 111kW [11]. In consequence, a maximal value of 20% of energetic

input should be available for recuperation into the process<sup>1</sup>.

This energetic estimation from thermodynamical data for the involved reactions is confirmed by our recorded energy balance during the experiments. The cooling trap for water condensation requires a power for the thermocirculator of 5kW, when a flow of 10Nm<sup>3</sup>/h real flue gas, respectively 7.4Nm<sup>3</sup>/h H<sub>2</sub> is realized, for instance. With respect to the energy for the corresponding H<sub>2</sub> production, 37kW, around 14% of energetic input for hydrogen production is generated by the reaction and could be usable for further system integration.

Our product gas is a lean gas with a mean gross caloric value of 5.74 MJ/Nm<sup>3</sup>, due to the high content of nitrogen (figure 7). With a surplus of hydrogen, this caloric value is improved up to 8.75MJ/Nm<sup>3</sup>. On one hand, further investigations for a transition into rich gas are necessary. Opportunities are the separation of nitrogen by pressure swing adsorption or polymer membranes, before methanation [19].

## 4 Summary, Conclusion

We show the proof of principle for the direct methanation of CO<sub>2</sub> content in flue gas at a lignite power plant. Without further preconditioning of the flue gas, the CO<sub>2</sub> is directly converted to methane via catalysis, which resulted in a conversion and a selectivity for methane both of up to nearly 100%.

Commercial nickel based catalysts are used and shows no degeneration during the measurement time.

The reaction needs no external energy supply. The oxygen content of 4-6vol% in the flue gas is burned by the hydrogen oxygen reaction and provides the thermal balance required for the Sabatier reaction.

The product gas from direct flue gas methanation exhibits a mean gross caloric value in a range of 6MJ/Nm<sup>3</sup>, which ranks it among the lean gases.

This lean gas is available as fuel. For a rotary engine, this is already shown by experiments at our chair [10]. The aim is to complete the power-to gas-to power circle with a chemical storage as methane and back electrification in times with lower regenerative energy production.

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<sup>1</sup>The data in Table 1 are calculated without compensation of oxygen, for a hydrogen production with 100kW.

Also we have the oxygen production during electrolysis. This oxygen could be involved again into the burning process of our product gas. In such a case, the gross caloric value increases and represents approximately the gross caloric value for pure methane, burned in air. Beside a possible recuperation of exothermal heat production, such a reuse of oxygen could improve the efficiency of the direct methanation.

Of course, a problem for the process of direct methanation is the high volume of the product gas. We have to transport and store all its nitrogen content. This causes additional energy losses and costs.

In consequence, further concepts for an efficient system integration are required, with a reuse of the oxygen generated by electrolysis and a recuperation of the heat generated by the methanation, for instance as energy for electrolysis. Nevertheless, the approach of direct methanation of flue gases is very interesting for plants in a smaller scale than for power plants, for example cement production or refineries.

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