

Novel methanation concepts for the production of Substitute Natural Gas

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Abstract

Methanation of CO and/or CO₂ is one promising way to convert renewable energy sources into established fuels such as substitute natural gas (SNG). Nevertheless, methanation raises several issues such as reaction heat removal, catalyst deactivation or the limitations in dynamic operation. A combination of innovative methanation reactor concepts, a three-phase methanation and a honeycomb methanation reactor, can make up for all these issues. The three-phase methanation carries out most of the CO/CO₂ conversion to CH₄ while acting as guard bed related to poisoning material (e. g. H₂S) for the following honeycomb reactor catalyst. Furthermore, the isothermal operating conditions of the three-phase methanation reactor enable easier removal of the heat of reaction as well as the benefit of insensitivity to load changes which might occur especially in power to gas (PtG) applications. In the honeycomb methanation, full conversion can be achieved. By adjusting the temperature profile inside the reactor, a high reaction rate can also be achieved.

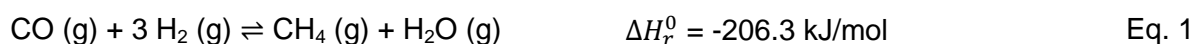
1 Introduction

In Europe recent focus has been made on developing alternative and renewable fuels to replace depleting fossil fuels like oil and natural gas. One solution is to use syngas from biomass gasification plants as feedstock for a methanation reactor. Another possible alternative is to carry out the methanation reaction using a CO₂ source (renewable or fossil) and a renewable H₂ source. In both cases, the resulting substitute natural gas (SNG) can be injected into the existing gas distribution grid or into gas storages and can be easily utilized in the well-established facilities and infrastructures.

For this publication, an innovative combination of two methanation reactor concepts, which can be implemented for both CO and CO₂ methanation or any combination thereof while satisfying the criteria for injection to the German gas grid, is presented.

2 Methanation process

CO and CO₂ methanation reactions (Eq. 1 and Eq. 4, respectively) are typically operated at temperatures between 250 °C and 700 °C and at pressures ranging from 1 bar to some tens of bars. Following Le Chatelier's law, high pressures and low temperatures are favorable with regards to maximizing methane production at equilibrium. Several metals such as Ni, Ru, Rh and Co can be used as catalytic active material for methanation, but most often Ni is seen as the optimum catalyst considering activity, CH₄ selectivity, and price [1, 2].



Since most syngases from gasification processes contain too few hydrogen even for sole CO-methanation (necessary: H₂/CO = 3 or more, typical values in gasification gases are below 2), an additional catalytic step is required to increase the hydrogen amount through shift reaction (Eq. 3). The lack of H₂ for methanation becomes even more imminent, when the process aims at CO₂ methanation (Eq. 4). A possibility is the addition of H₂ from other sources like electrolysis of water with regenerative power.

The reaction kinetics of the CO methanation is faster than that of the CO₂ methanation, but contrary to CO₂ methanation, CH₄ selectivity is not 100 % and catalyst deactivation through carbon deposition via Eq. 2 is a well-known issue [3–6]. Catalyst poisoning with sulfur is also a well-known deactivation phenomenon and the methanation reactant gas should therefore be purified from any traces of sulfur before entering the methanation reactor [5].

It is technically possible to combine CO and CO₂ methanation in one reactor. However, studies have shown that only a few ppm of CO in the methanation reactor feed gas can impede the CO₂ methanation reaction [7]. This leads to a preferential methanation of CO with H₂ (Eq. 1) before the CO₂ methanation (Eq. 4) can even start.

Since both CO and CO₂ methanation are highly exothermic reactions, one main issue of methanation processes is an efficient removal and utilization of the heat of reaction in order to prevent thermodynamically limited carbon conversion as well as catalyst sintering.

The methanation process development at the Engler-Bunte-Institute resulted in two innovative processes which help to overcome the aforementioned limitations: the three-phase methanation (3PM) and the honeycomb methanation (HCM).

3 Innovative methanation concepts

3.1 Three-phase methanation (3PM)

The **3PM reactor** is a slurry bubble column reactor filled with a heat transfer liquid in which fine catalyst particles are suspended by the rising gas bubbles (see Figure 1). The presence of the liquid-phase with its high heat capacity and high thermal conductivity allows for effective and accurate temperature control: the heat of reaction can be completely removed and the reactor can be operated almost isothermally. In addition, the slurry reactor concept enables continuous catalyst exchange during operation. This is of significant importance when dealing with potentially deactivating catalysts like Nickel. Furthermore, even under dynamic operating conditions isothermal mode of operation is possible [8, 9].

Drawbacks of the 3PM reactor are the heat transfer liquid thermal stability, which limits the reactor temperature, as well as the additional gas / liquid mass transfer resistance.

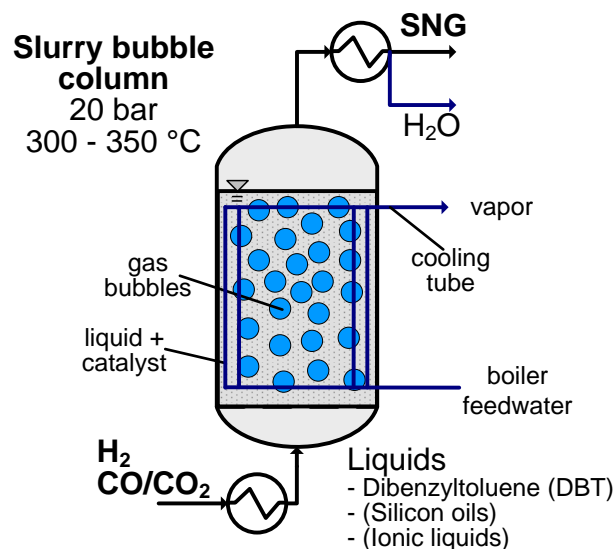


Figure 1: Schematic of a three-phase methanation reactor.

In Figure 2, the conversion of CO and CO₂ (X_{CO} and X_{CO_2} respectively) is compared. As mentioned before, the CO methanation is faster than that of the CO₂ methanation resulting in much higher conversions at the same conditions. Furthermore, it can be seen that high pressures are advantageous for achieving high conversion rates at a constant reactor volume. Elevated pressures improve the gas/liquid mass transfer as well as the intrinsic reaction rate. High CO and CO₂ conversions (not shown here) are feasible within the 3PM reactor. However, $X_{CO_2} > 95\%$ are difficult to obtain. To reach higher X_{CO_2} a second methanation step would be necessary.

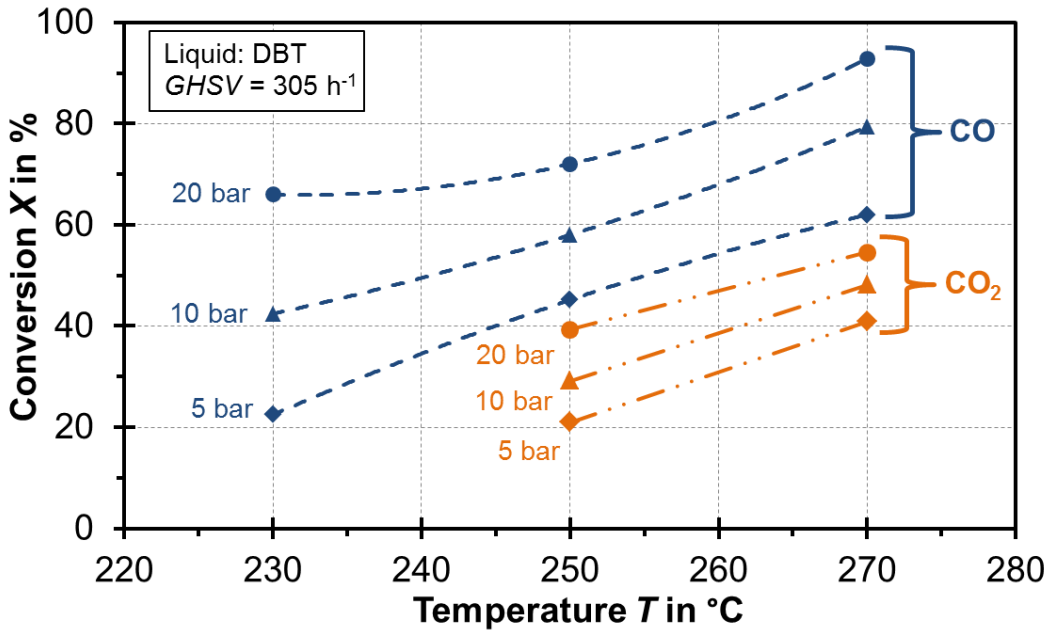


Figure 2: Comparison of the temperature dependencies of the CO and CO₂ conversion in the three phase methanation reactor ($\tau_{mod} = 80 \text{ kg}\cdot\text{s/mol}$).

Figure 3 shows the dynamic behavior of the 3PM reactor after a gas velocity step change. The reactor reset time is independent of the reactor hydrodynamics or reaction kinetics: the reset time depends only on the gas velocity, while the reactor temperature stays constant. This demonstrates that the 3PM reactor is particularly adapted for dynamic operating conditions.

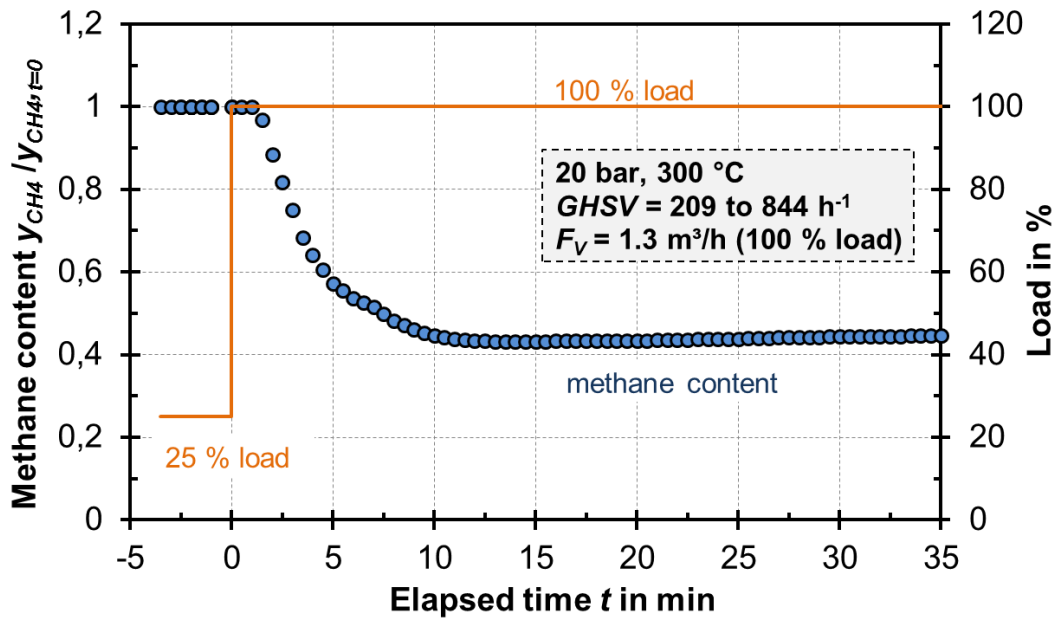


Figure 3: Evolution of the methane content at the 3PM reactor outlet after a gas load step change.

3.2 Honeycomb (HCM) methanation

As described above, a second methanation reactor downstream the three phase methanation is required for very high conversions. The **HCM reactor** is well suited for this application. It is packed with honeycomb structures – often called monoliths - which are impregnated with catalyst. These honeycombs are systems of cooled parallel channels which offer advantages compared to the established reactor systems (Figure 4). The high heat conduction allows controlling the temperature inside the reactor. As a consequence, a high temperature at the inlet (to have a high reaction rate) and a low temperature (because of equilibrium limitations) at the outlet can be achieved. Furthermore, abrasion and pressure drop of the monoliths are very low and the adjustable geometric parameters of the monoliths offer the possibility to realize new reactor concepts.

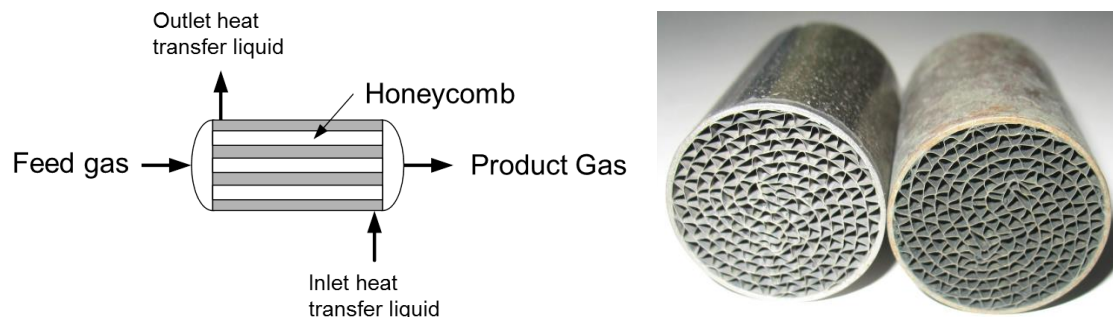


Figure 4: Schematic of a honeycomb methanation reactor

Developments to the HCM process achieved at the Engler-Bunte-Institut are shown in the following figures. Figure 5 shows the conversion of CO as a function of the reactor temperature for an over-stoichiometric H_2/CO -Feed. With a wall temperature of 260 °C, the CO conversion reaches almost 100 %. The hotspot temperature in the honeycomb-reactor is about 49 K above the reactor temperature accelerating the reaction rate. Fixed-bed reactors have a significantly higher hotspot-temperature, which is very close to the adiabatic temperature. The selectivity increases with increasing temperature up to 98 % (in the investigated range). As byproducts, CO_2 as well as higher hydrocarbons produced by Fischer-Tropsch synthesis can be detected.

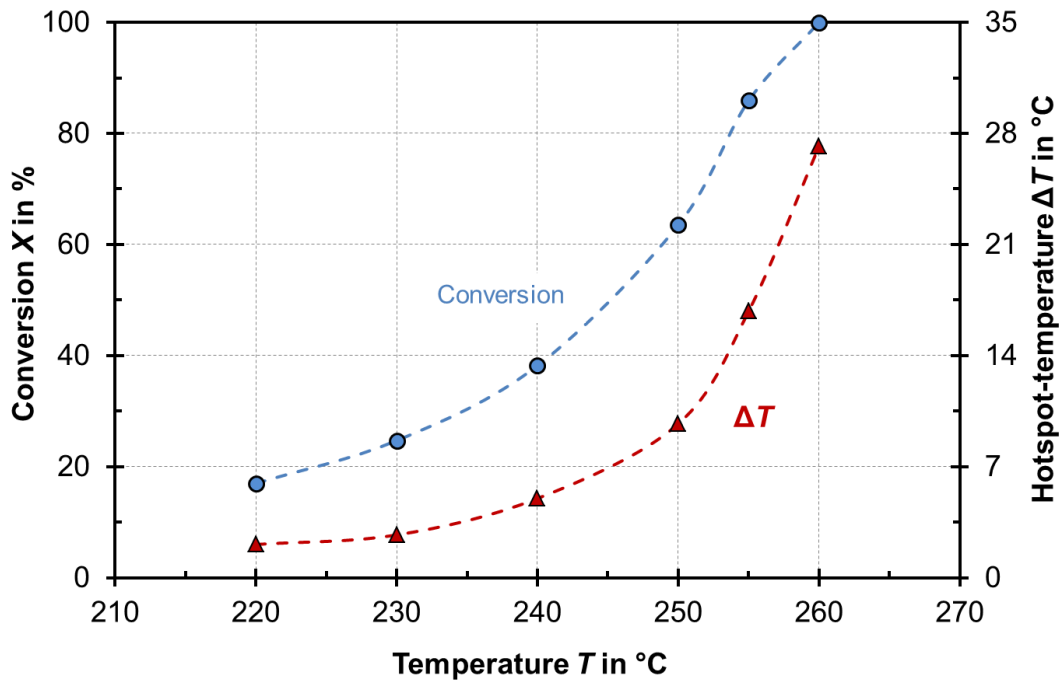


Figure 5: Temperature dependency of CO conversion in the EBI honeycomb methanation reactor (8 bar)

Figure 6 shows the CO₂-conversion as a function of the reactor-temperature and the hotspot-temperature in the honeycomb. Reaching a wall temperature of 300 °C the CO₂ conversion reaches 98.4 %. For the whole temperature-range up to 300 °C the selectivity is nearly 100 %. The CO₂-methanation is limited thermodynamically at temperatures below 300 °C.

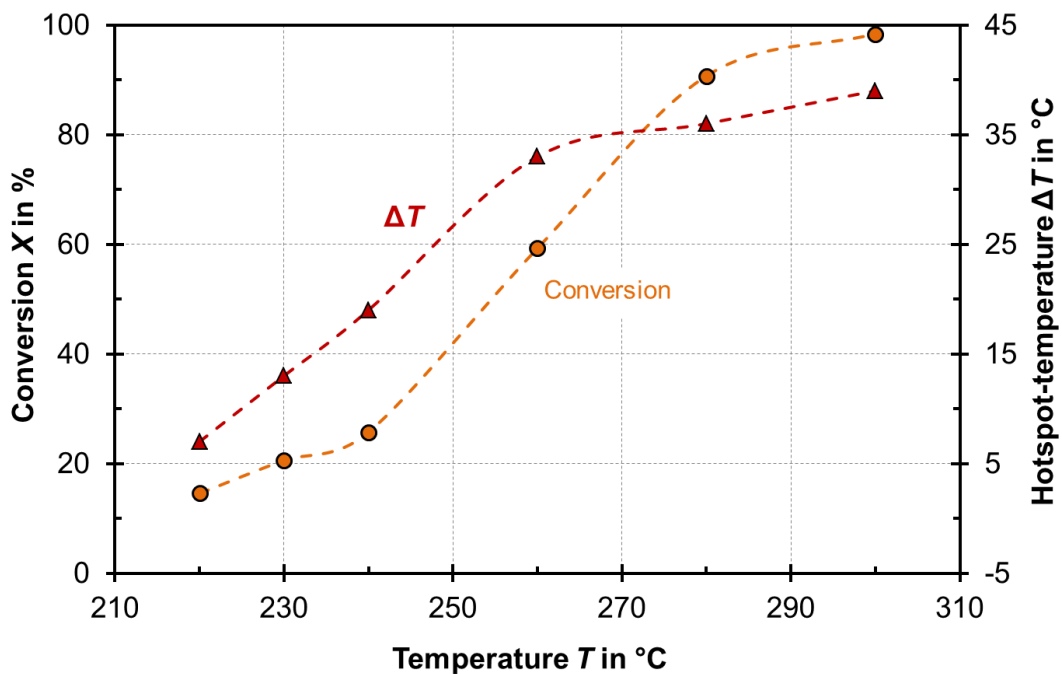


Figure 6: Temperature dependency of the CO₂ conversion in the honeycomb methanation reactor (8 bar)

4 Reactor combination

In the following, the combination of a 3PM reactor followed by a HCM reactor will be introduced offering an elegant way to address the issues related to high conversion, reaction heat removal, catalyst deactivation and dynamic operation. This combination is illustrated in Figure 7.

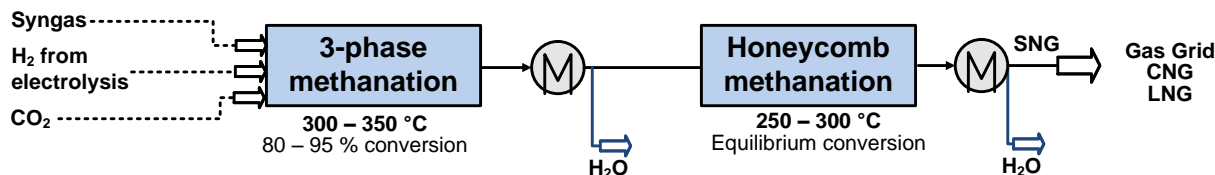


Figure 7: Innovative methanation concept: combination of three-phase methanation (3PM) with honeycomb methanation (HCM) (here: CO₂-methanation).

The carbon oxides (CO and/or CO₂) and the required H₂ stream with a sufficient stoichiometry are first sent through a 3PM reactor. In this reactor, the methanation reaction can be carried out at a defined temperature and under nearly isothermal reaction conditions. Furthermore, most of the heat of reaction can be easily removed. The 3PM is tolerant to fast changes in reactor load in a wide range which makes it very applicable for PtG applications. Additionally, if the catalyst undergoes deactivation due to sulfur poisoning or carbon deposition, it can be replaced during operation. If the carbon oxides have not already been fully converted in the 3PM reactor, the gas leaving this reactor is cooled down in order to condensate and remove water. Removing water before the second reactor helps to overcome the thermodynamic limitations. Then, the gas is fed to the second methanation reactor, the HCM reactor, which is used to achieve high conversion of the carbon oxides at polytropic conditions in order to obtain SNG with methane content above 95 %. Load changes and changing feed gas compositions are buffered by the 3PM, while the HCM assumes the role of product shaping in a robust and uncomplicated reactor system. Latent deactivation of the HCM catalyst will not occur as all poisonous impurities like sulfur components were trapped in the 3PM and most of the CO should have already been converted in the 3PM reactor. Hence, this configuration uses the specific properties of both reactors to compensate their weak points which results in a very efficient SNG production.

5 Conclusion

SNG production via methanation is a promising way to transform and store energy from renewable sources. Nevertheless, methanation shows several issues related to reaction heat removal, catalyst deactivation and dynamic operation. These problems can be tackled by implementing innovative methanation reactor concepts like the 3PM or the HCM reactor. A combination of these two reactors is especially effective to solve these issues, while delivering a gas product fulfilling the SNG quality requirements.

With the envisaged combination of 3PM and HCM a very robust process for SNG production out of CO and/or CO₂ containing feed gases is available. The combined methanation reactors and a subsequent final drying lead to a high quality SNG for injection to the gas grid. This reactor combination can be operated at steady state as well as at dynamic conditions (fluctuating carbon and H₂ sources). The 3PM reactor acts as buffer for load changes and as a filter for the following HCM. The HCM is used in order to reach the requirements for injection to the gas grid without the need for costly gas separation units or gas recycles.

6 References

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7 Nomenclature

Symbol	Unit	Name
F_V	m ³ /h	Volume flow at 0 °C and 1,013 bar
$GHSV$	h ⁻¹	Gas Hourly Space Velocity
p	bar	Pressure
T	K, °C	Temperature
X_i	-	Conversion of gas i
y_i	-	mole fraction (gas phase)
ΔH_r^0	kJ/mol	Reaction enthalpy at normal conditions
τ_{mod}	kg·mol/s	Modified residence time (mass of catalyst divided by the mole flow of CO or CO ₂)