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# Direct catalytic methanation of biogas (DMB): From laboratory experiments to demonstration scale

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## Motivation:

DMB facilitates biogas upgrading to biomethane ($CH_4 \geq 95\%$) without the separation of $CH_4$ from $CO_2$
[Conventional biomethane production: separation, e.g. by pressure swing absorption [1] (and subsequent $CO_2$ methanation [2])]
⊕ Simplified upgrading process using $CO_2$ for small-, medium- and large-scale biogas and waste water treatment plants
⊖ Methanation with high reactant $CH_4$ concentration is prone to catalyst deactivation due to carbon formation (Fig. 1)

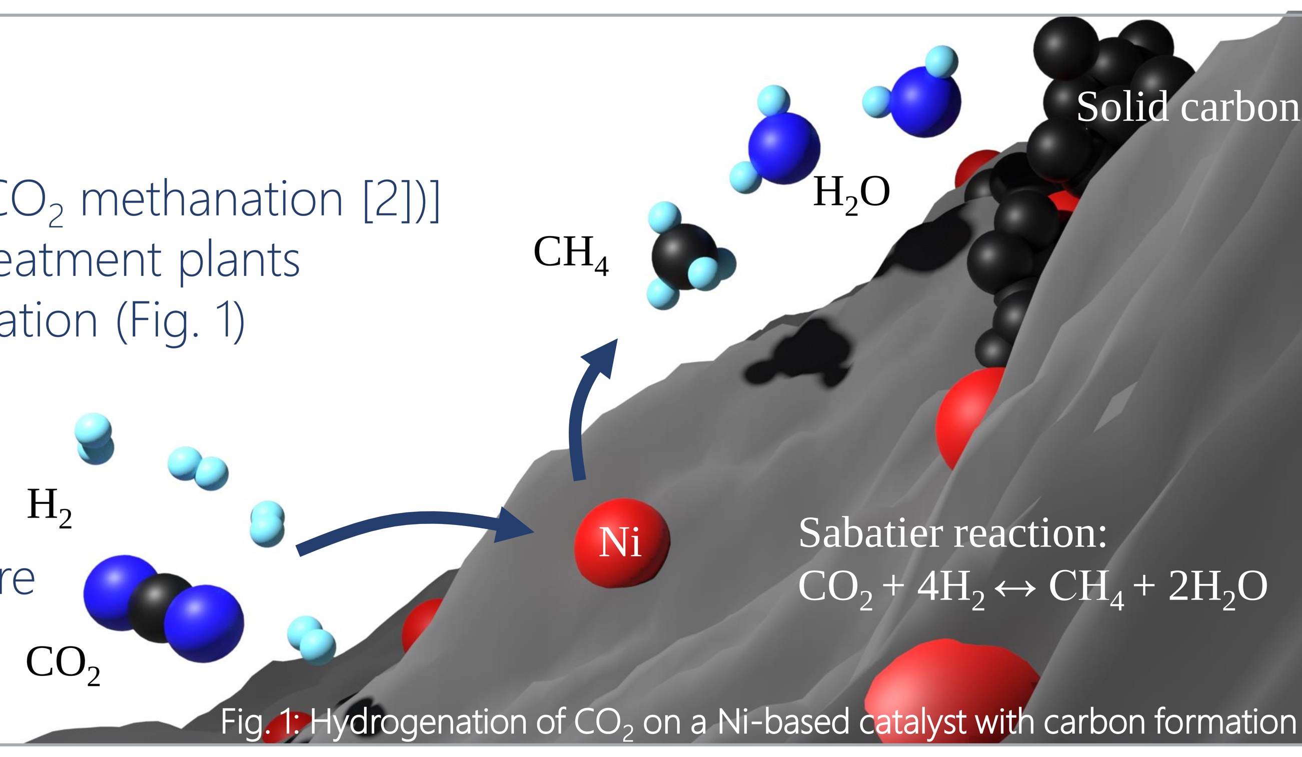

Fig. 1: Hydrogenation of $CO_2$ on a Ni-based catalyst with carbon formation

## Objectives:

- Identification of operational constraints of DMB with respect to carbon deposits
- Performance analysis of semi-commercial $Ni/Al_2O_3$ catalysts with varying biogas composition and pressure
- Process optimisation in terms of product gas quality, i.e. $CH_4$ product gas concentration
- Development of an enhanced process design for demonstration on industrial sites

## Methods:

- Thermochemical analysis of carbon formation:
  Determining the chemical equilibrium by means of Gibbs energy minimisation using the software CEA [3]
- Experimental analysis of two different semi-commercial $Ni/Al_2O_3$ catalysts on a 1 kW fixed bed reactor (Fig. 2):
  - Investigation of synthesis temperature for biogas $CH_4/CO_2$ ratios of 0.4 to 4 and operating pressure of 1.5 $bar_{abs}$ and 4.5 $bar_{abs}$
  - Examination of the susceptibility of the catalysts to form carbon

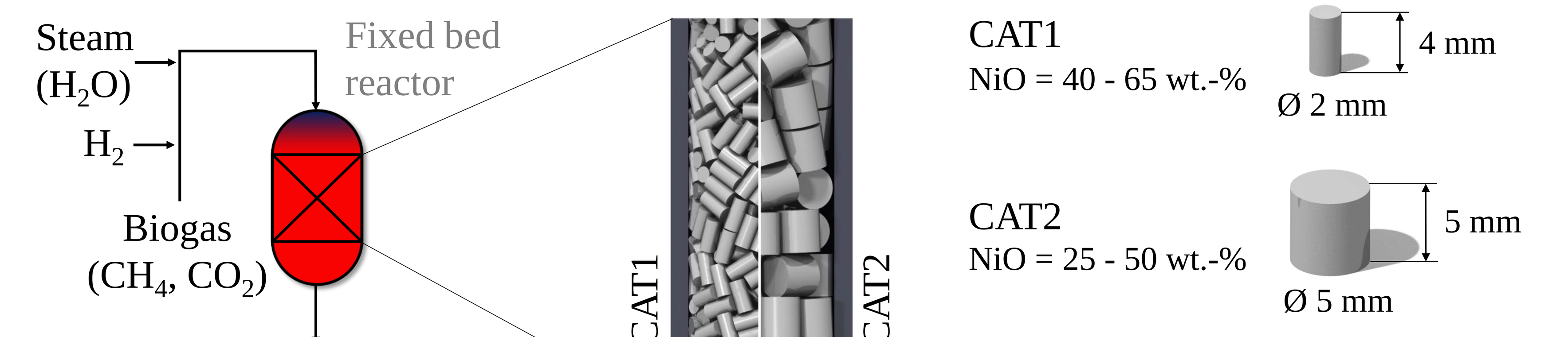

Fig. 2: Schematic diagram of the 1 kW reactor setup (a) with the catalysts used (b)

- Laboratory experiments with a two-stage 5 kW methanation process with intermediate condensation and catalyst CAT1 (Fig. 3)

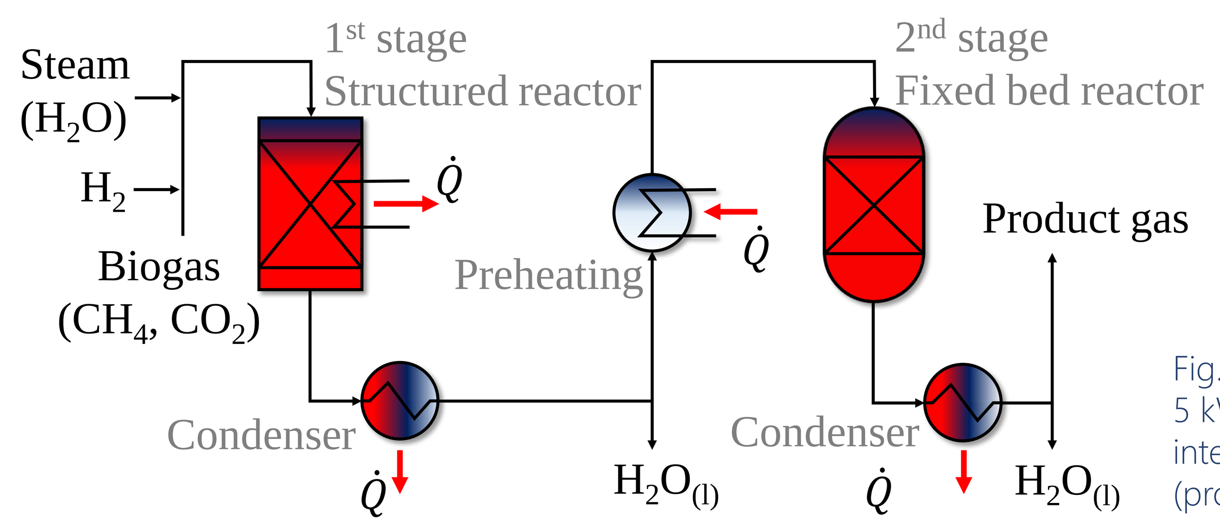

Fig. 3: Schematic diagram of the two-stage 5 kW methanation process with intermediate condensation (process design according to [4])

## Outlook:

- The two-stage design will be transferred to a 20 kW demonstration plant (Fig. 7) which will test DMB at industrial sites (biogas and waste water treatment plant [5])
- Data obtained from $T_{crit}$ analysis will be used for process optimisation:
  High peak temperature improves process limiting reaction kinetics while $T < T_{crit}$ prevents carbon formation

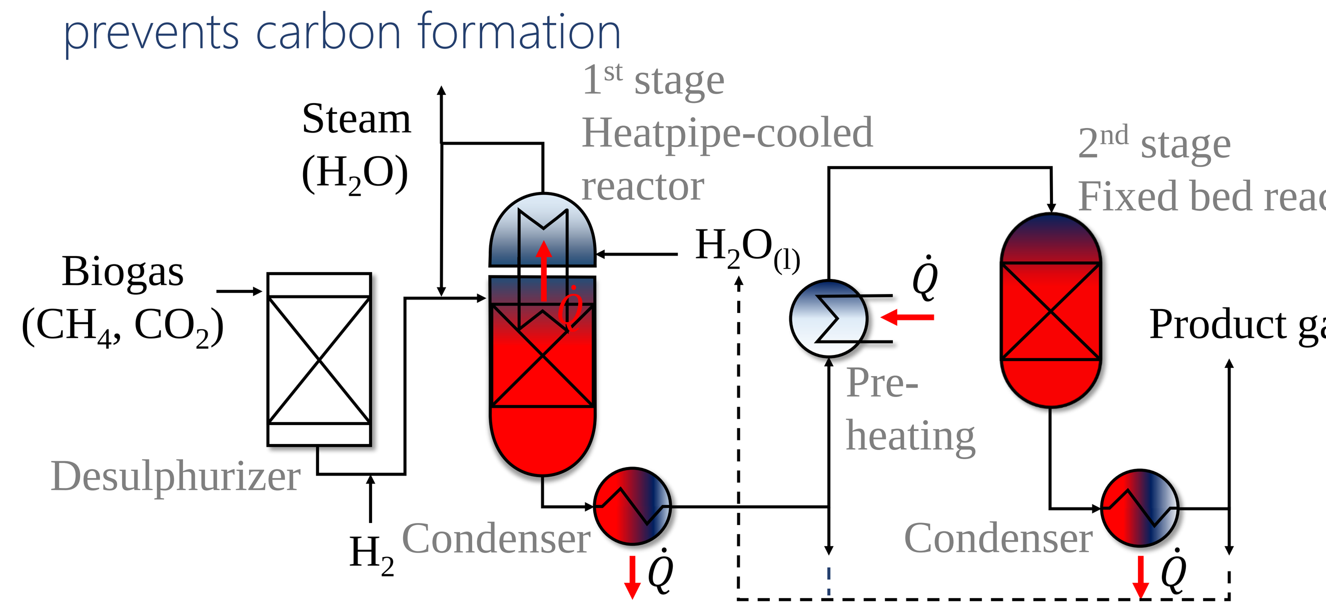

Fig. 7: Schematic diagram of the two-stage 20 kW demonstration plant with integrated steam generation and intermediate partial condensation

## Results:

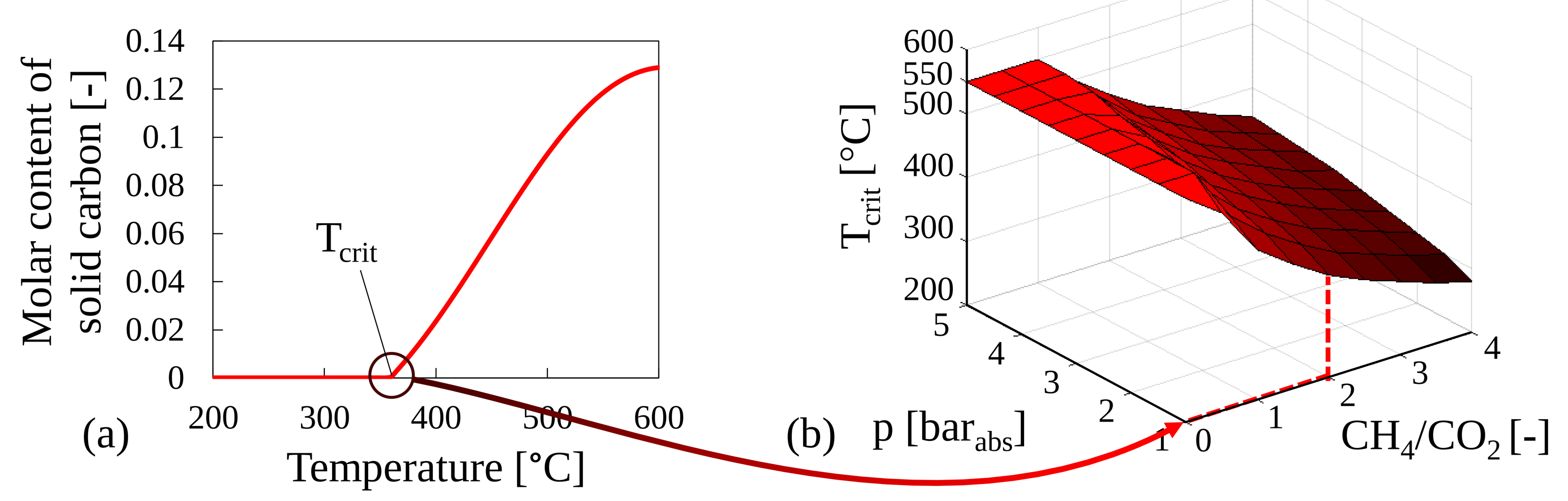

Fig. 4: Formation of solid carbon in chemical equilibrium dependent on temperature (a) as well as the critical temperature for carbon deposition $T_{crit}$ dependent on pressure **p** and the biogas $CH_4/CO_2$ ratio (b)

- Carbon deposits above the critical temperature $T_{crit}$ (Fig. 4a) which increases with increasing pressure and decreasing reactant $CH_4$ concentration (Fig. 4b) as well as higher steam content (data not shown)

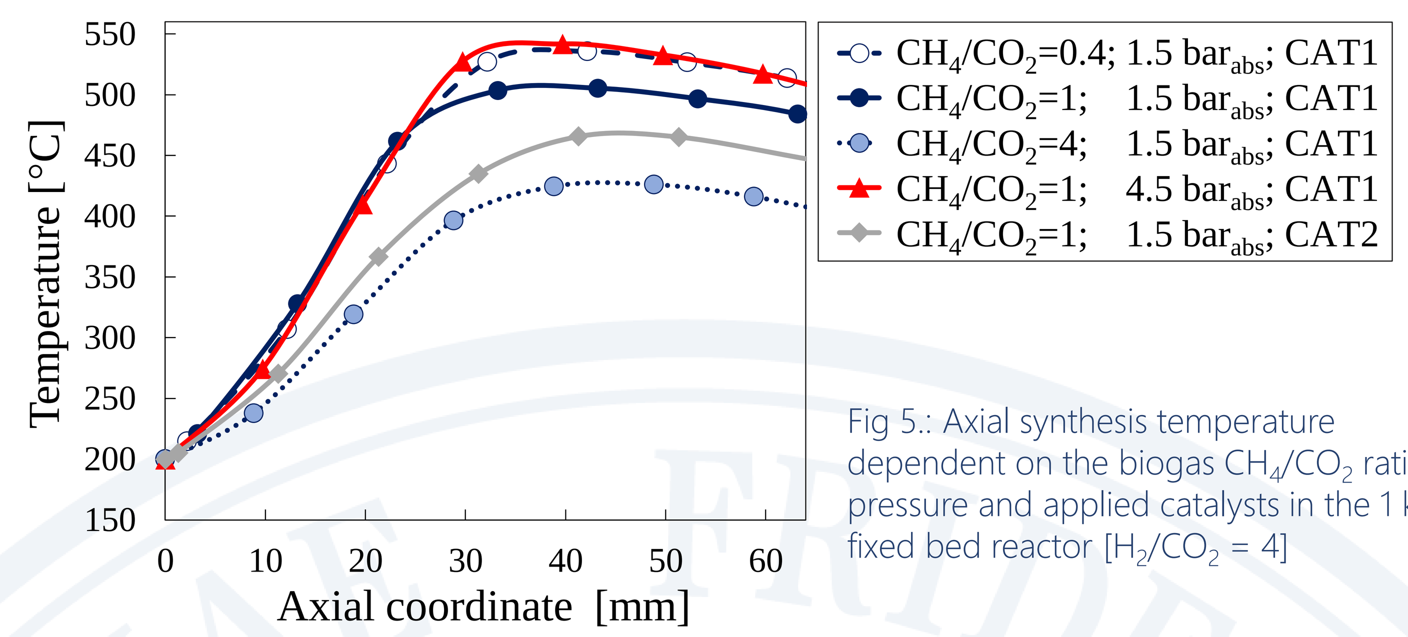

Fig 5.: Axial synthesis temperature dependent on the biogas $CH_4/CO_2$ ratio, pressure and applied catalysts in the 1 kW fixed bed reactor [$H_2/CO_2 = 4$]

- Higher $CH_4/CO_2$ and lower pressure reduces the heat released during exothermic methanation reaction (Fig. 5)
- A fixed bed with CAT1 features higher activity and robustness against carbon formation (data not shown)

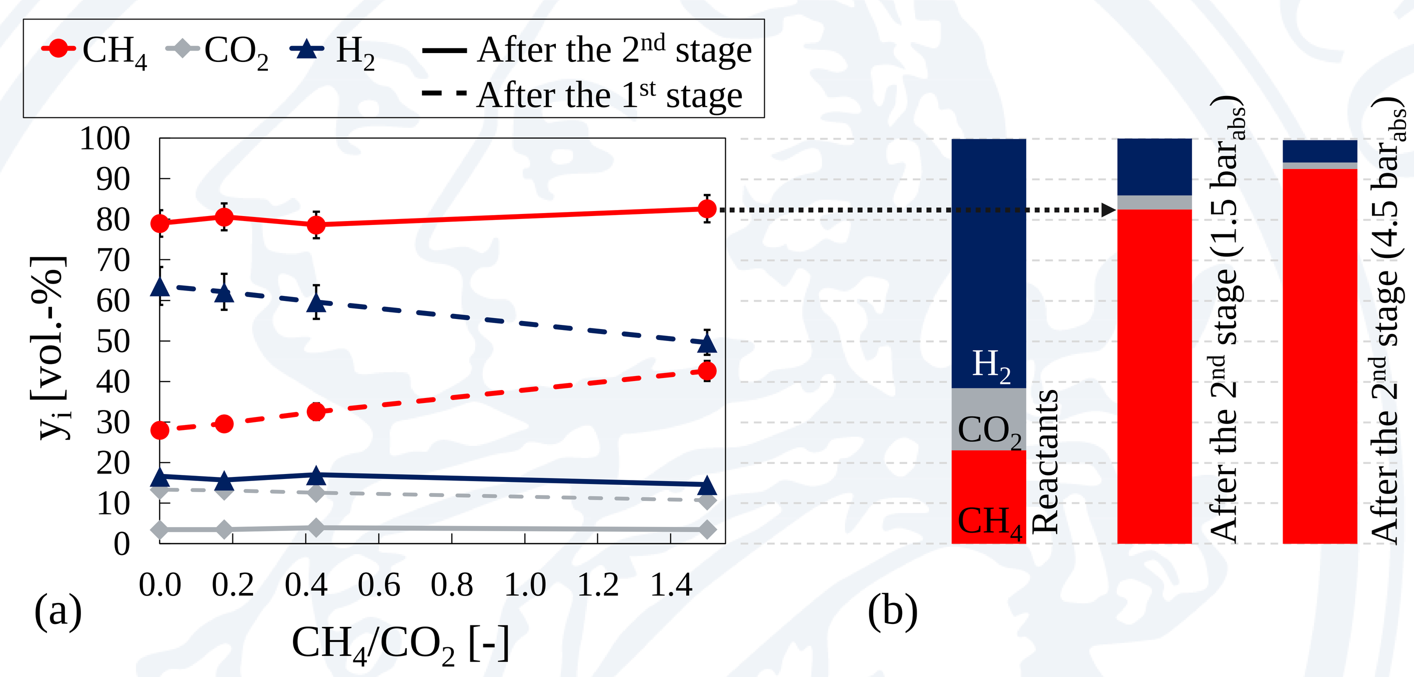

Fig. 6: Dry gas-phase species concentration $y_i$ dependent on the biogas $CH_4/CO_2$ ratio (a) as well as the reactant and product gas concentrations for a biogas CH4/CO2 ratio of 1.5 at two different pressure levels (b) [$H_2/CO_2 = 4$; Reactant steam content $y_{H_2O}$=18 vol.-%; Catalyst = CAT1]

- The two-stage process achieves almost constant product gas quality irrespective of the biogas composition (Fig. 6a)
- DMB operation at elevated pressure achieves product gas $CH_4$ concentrations of up to 93 vol.-% after the 2nd stage (Fig. 6b)

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[1] Fachagentur Nachwachsende Rohstoffe e. V. (2014). Leitfaden Biogasaufbereitung und –einspeisung.
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[4] Neubert, M., Hauser, A., Pourhossein, B., Dillig, M., & Karl, J. (2018). Experimental evaluation of a heat pipe cooled structured reactor as part of a two-stage catalytic methanation process in power-to-gas applications. Applied Energy, 229, 289-298.
[5] Power-to-Biogas project (funding code: 03KB165A) and Kläffizient project (funding code: 03EI5421A). www.evt.tf.fau.de.

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