

Research article

Unsteady-state methanation of carbon dioxide in a fixed-bed recycle reactor – Experimental results for transient flow rate ramps

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ABSTRACT

The utilization of fluctuating renewable electrical energy in chemical processes necessitates the dynamic operation of chemical reactors. One important example is the methanation reactor in the power-to-gas process, where the electrolysis of water is applied for the production of hydrogen, which can be converted into methane via hydrogenation of carbon oxides. The methanation step might be operated dynamically in order to reduce the storage capacity of hydrogen. Therefore, the unsteady-state behavior of the methanation is investigated in the present work. In particular a fixed-bed reactor with product recirculation is considered in terms of the system stability upon dynamic variations of the inlet flow rate. A systematic three-step study based on a steady-state parameter variation as well as load ramps with and without gas recycle was conducted on a lab-scale test facility. Focusing on a reactor system reaching chemical equilibrium, it was found that the reactor behavior is independent of the load change velocity in the investigated range. During the transient variation of the inlet volume flow rate, the temperature response inside the fixed-bed is decelerated compared to the concentration response. The adaption of the product recirculation allows to stabilize the bed temperature, which is unavoidable for a high conversion of carbon dioxide.

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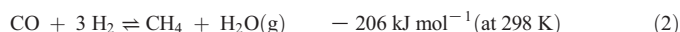
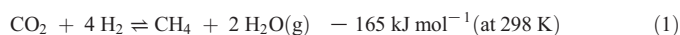
1. Introduction

The power-to-gas process (PtG) [1,2] is applied to store fluctuating wind and solar power as synthetic natural gas (SNG). Thereby, the electrical energy is used to produce hydrogen in an electrolysis unit. Downstream, the hydrogen is converted to methane via the hydrogenation of carbon dioxide (methanation). The upgraded SNG can be stored in the existing infrastructure, e.g. in the gas grid, and utilized on demand.

Due to the fluctuating renewable electricity input, the hydrogen supply of the electrolysis is generally unsteady. Therefore and due to high investment costs of hydrogen storage systems, a flexible operation of the methanation is favored [3,4]. Especially, concepts with a product gas recirculation are proposed for a flexible operation of fixed-bed methanation reactors. The product recirculation cools the fixed-bed by diluting the inlet gas and prevents the sintering of the catalyst. Furthermore, the process can be controlled by the flow rate of the product recirculation.

The hydrogenation of carbon dioxide (Eq. (1)), being a linear combination of carbon monoxide hydrogenation (Eq. (2)) and the reverse

water–gas shift (Eq. (3)), is highly exothermic and usually catalyzed with nickel as active material. High pressures and low temperatures shift the chemical equilibrium towards the products of the methanation reactions. Various fundamental aspects of the methanation have been reviewed [5–7].



The most comprehensive study on the unsteady-state methanation without product recirculation was conducted by van Doesburg and de Jong [8,9]. The authors studied disturbances of the feed temperature and concentration for binary (H_2 and either CO or CO_2) as well as ternary (H_2 , CO , and CO_2) syngas mixtures. The results comprise the inhibition of the carbon dioxide methanation in the presence of carbon monoxide and a fast concentration response compared to a slow temperature response. In addition, the wrong way behavior was discussed

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by van Doesburg and de Jong. This effect is caused by the influence of inlet temperature disturbances on the conversion in the first part of the catalytic bed, which leads to an opposite transient temperature behavior in the second part of the bed.

Güttel [10] simulated the periodic operation of the carbon monoxide methanation. In the study the inlet composition was varied between stoichiometric and equimolar case. A self-stabilizing system behavior was observed for high switching frequencies. Further unsteady-state scenarios were simulated for biogas upgrading with electrolytically produced hydrogen [11], for SNG production of coal syngas [12] and for life-support systems using metabolic carbon dioxide in a space station [13].

Rönsch et al. [14] showed that a disproportional adaption of the recycle flow rate is required to prevent the overheating of an adiabatic fixed-bed reactor. The results are in agreement with the experiences of the ADAM I pilot plant [15], where SNG is produced by the TREMP process consisting of three adiabatic fixed-bed reactors with intermediate cooling and a product recirculation after the first reactor. Harms et al. [15] found out that unexpected process disturbances and the load changes of the syngas from 100 to 50% could be handled by an extensive process control system at the TREMP process.

Li et al. [16] analyzed the stability of a cooled fixed-bed reactor with mass recycle by the recirculation of product gas and heat recycle by preheating the coke oven gas upstream the methanation. The reactor system needed approximately 1 h to reach a new steady-state of the reactor temperature if the inlet molar fraction of carbon monoxide is varied stepwise up to 2 mol% only. Additionally, the authors used a linearized simulation model to prove that the system stability is lowered by the recirculation of heat, mass, or both at the same time.

In the present paper, the unsteady-state behavior of a fixed-bed recycle reactor is analyzed systematically by dynamic experiments with and without product recirculation. Before a steady-state parameter variation was conducted. The study is limited to the volumetric flow rate of the diluted syngas at the system's inlet as the dynamically varied parameter and its effect on carbon dioxide conversion and bed temperature. The syngas ratio was fixed at stoichiometric composition ($\varphi_{H_2}/\varphi_{CO_2} = 4$). The approach represents a first step to understand the load-flexibility of a polytropic methanation reactor.

2. Experimental methods and methodology

2.1. Experimental setup

In the fixed-bed reactor, the commercial catalyst Meth134, 20Ni/5CaO/75Al₂O₃, was used being the same as analyzed in Köchermann et al. [17]. 1 g of the ground and sieved fraction of 0.5 to 1.0 mm was utilized for each experiment. The temperature of the catalyst should be limited to 510 °C for long term operation and to 700 °C for short term operation. To reduce the nickel oxide, the catalyst was activated with an inlet gas composition of 10 vol.% H₂ in N₂ and a constant flow rate of 1 L min⁻¹ (STP). Thereby, the fixed-bed was heated up to 480 °C with a ramp of 3 K min⁻¹ and held isothermal for another 4 h. Afterwards the reactor was kept inert by purging with nitrogen. In a continuous test for more than 8 h, the stability of the catalytic activity was confirmed by constant outlet concentrations as well as a constant temperature profile in the reactor.

The experimental setup of the fixed-bed reactor is shown in Fig. 1. A moveable thermocouple with a protection tube (outer diameter of 3 mm) was placed in the center of the reactor (internal diameter of 13 mm). The axial position of the thermocouple is specified along the gas-flow direction through the fixed-bed with a value of zero at the beginning of the catalytic bed according to the scale in Fig. 1. The undiluted catalyst bed had a height of 1.2 cm and was placed 14.2 cm downstream the reactor inlet to allow for sufficient gas pre-heating. Aluminum oxide with a particle diameter of 1 to 3 mm was used as inert material. A blank experiment with inert material only was performed to rule out blind activity in the system.

Furthermore, Fig. 1 shows the lab-scale test facility as well as the measured (white background) and controlled (gray background) process variables. The syngas mixture (N₂, H₂ and CO₂) was generated by mass flow controllers (El-Flow® from Bronkhorst). Subsequently, the syngas was pre-heated to ca. 220 °C prior to entering the reactor, which was heated by a split tube furnace. Downstream the methanation reactor, water was separated from the gas stream in a condensation trap at a temperature of 20 °C. The product gas was partly recycled by a compressor (HMZ 030 from K-Engineering). The recycle flow rate was

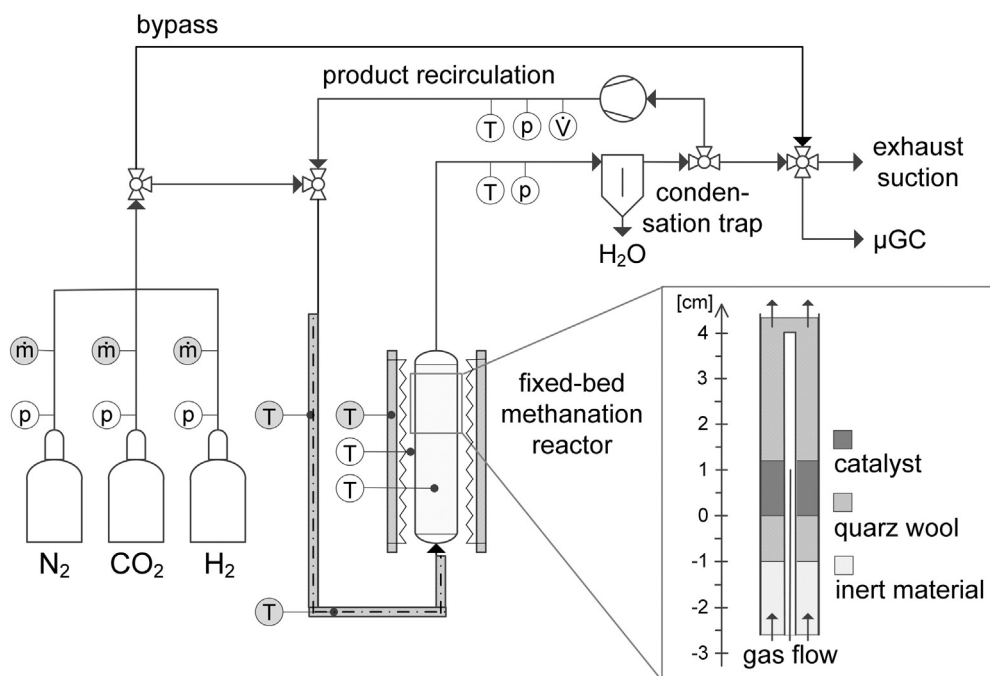


Fig. 1. Flow sheet of the lab-scale test facility with the catalyst arrangement in the reactor and the evaluated process values.

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