



# Improvement of three-phase methanation reactor performance for steady-state and transient operation



Jonathan Lefebvre<sup>a,\*</sup>, Manuel Götz<sup>b</sup>, Siegfried Bajohr<sup>a</sup>, Rainer Reimert<sup>a</sup>, Thomas Kolb<sup>a</sup>

<sup>a</sup> Karlsruhe Institute of Technology, Engler-Bunte-Institut I, Fuel Chemistry and Technology, Engler-Bunte-Ring 1, 76131 Karlsruhe, Germany

<sup>b</sup> DVGW-Forschungsstelle at the Engler-Bunte-Institut of the Karlsruhe Institute of Technology (KIT), Engler-Bunte-Ring 1, 76131 Karlsruhe, Germany

## ARTICLE INFO

### Article history:

Received 8 September 2014

Received in revised form 20 October 2014

Accepted 27 October 2014

Available online 13 January 2015

### Keywords:

Methanation

SNG

Three-phase methanation

Liquid phase hydrogenation

Slurry bubble column reactor

Transient operation

## ABSTRACT

The performance of a slurry bubble column reactor was evaluated for its application as a methanation reactor. The influences of the reactor pressure (5 to 20 bar), temperature (275 to 325 °C), gas velocity (0.8 to 1.6 cm/s), catalyst concentration (1.6 to 9 vol.%) as well as reactant partial pressures ( $H_2/CO_2$  ratio from 3.8 to 6.3) on the reactor performance were assessed and optimal process conditions for substitute natural gas production were identified. An increase in pressure, temperature, and  $H_2/CO_2$  ratio improves the reactor performance. The optimal catalyst concentration depends on the operating conditions. Under the experimental conditions of the work presented in this paper, a concentration of 6.5 vol.% led to the highest conversion rates.

Additionally, the dynamic behavior of the three-phase methanation reactor was investigated using inlet gas velocity step changes to simulate load variation of a power-to-gas facility. The reactor showed rapid adaptation while maintaining an isothermal temperature profile.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

As a result of the continuous reduction of crude oil and gas resources, and the increasing concern for greenhouse effects due to human  $CO_2$  emissions, recent focus has been put on the development of renewable and environmentally friendly energy from wind and sunlight. As these energy sources are intermittent the produced electricity needs to be balanced for power grid stability purposes. Electricity storage via power-to-gas (PtG) technology is a promising solution to tackle this issue. The PtG process links the power and natural gas grids by the conversion of electrical energy into a chemical energy carrier, substitute natural gas (SNG). SNG is produced via two steps:  $H_2$  production through water electrolysis and  $H_2$  conversion with an external  $CO_2$  source into  $CH_4$  via the methanation reaction [1]. The resulting SNG can be injected into the existing gas grid or gas storages and can easily be utilized in the already well-established infrastructure and conversion systems. The methanation reactor used in a PtG facility needs to be highly load flexible in order to follow the  $H_2$  profile from the electrolyzer as closely as possible, thus keeping the  $H_2$  storage tank as small as possible, while satisfying SNG quality requirements. For small PtG plants, a slurry bubble column reactor (SBCR) is seen as a suitable methanation reactor type, since it allows for efficient reactor temperature control, as well as good dynamic behavior [2].

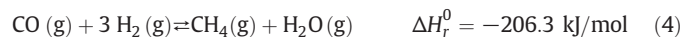
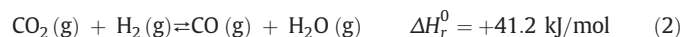
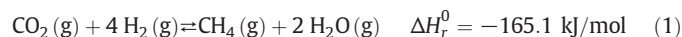
In this publication the application of a SBCR as a three-phase methanation reactor was investigated. First, the influence of the different

process variables on the  $CO_2$  conversion and  $CH_4$  formation rate were the focus. Whenever possible, optimum process conditions regarding high conversion and high space velocity were defined. In the second part the dynamic behavior of a three-phase methanation reactor was tested regarding the whole PtG process chain.

## 2. Fundamentals

### 2.1. Methanation

Different reactions are implied in the  $CO_2$  methanation process: the key reaction, the  $CO_2$  hydrogenation (Eq. (1)), is accompanied by other reactions such as the reverse water gas shift (Eq. (2)), the Boudouard (Eq. (3)) and the CO hydrogenation (Eq. (4)) reactions. Methanation reactors are typically operated at temperatures between 200 °C and 500 °C and at pressures ranging from 1 bar to approximately 100 bar.



\* Corresponding author. Tel.: +49 72160842568.

E-mail address: [jonathan.lefebvre@kit.edu](mailto:jonathan.lefebvre@kit.edu) (J. Lefebvre).

Reaction 1 is highly exothermic. Consequently, a main issue of the CO<sub>2</sub> methanation reactor is to achieve a good reaction heat removal to prevent a thermodynamic limitation of the CO<sub>2</sub> conversion and catalyst sintering. Several metals such as Ni, Ru, Rh, and Co may be used as catalytic active material for the CO<sub>2</sub> methanation. However, most often Ni is seen as the optimum catalyst choice considering its relatively high activity, good CH<sub>4</sub> selectivity, and low raw material price [3,4].

State-of-the-art reactor concepts for SNG production are two-phase reactors, e.g. adiabatic fixed-bed systems [5]. An alternative concept is fluidized bed reactors which have been tested in a number of pilot scale systems [6,7]. Adiabatic fixed-bed reactor concepts typically require 2–5 catalytic beds in series with inter-cooling and recycle streams, while fluidized-bed reactors offer a more effective heat removal with integrated heat exchanger tubes, but require abrasion resistant catalysts. When exposed to fluctuating feed streams, these two-phase reactors typically suffer a quick temperature change, as the cooling system cannot be adapted to a rapid change in reaction heat production [8]. This temperature drop can lead to catalyst cracking or sintering [9].

Another reactor concept is based on a three-phase reactor (e.g. SBCR) filled with a heat transfer liquid enabling effective and accurate temperature control (see Fig. 1). Due to the additional heat capacity of its liquid phase, a three-phase reactor is less prone to quick temperature changes in case of fluctuating feed streams. Furthermore, three-phase methanation enables catalyst removal during operation. This leads to a stable isothermal operation of the methanation process [2,10]. Possible drawbacks of a three-phase reactor include evaporation or decomposition of the heat transfer liquid as well as the additional mass transfer resistance due to the liquid phase. The discussed reactor types are compared in Table 1.

## 2.2. Slurry bubble column reactor (SBCR) basics

Since SBCR efficiency can be limited by the mass transfer resistance induced by the heat transfer liquid, it is of first importance to identify optimal operating parameters for maximized CO<sub>2</sub> conversion as well as CH<sub>4</sub> formation rate. For the three-phase methanation the following mass transfer steps can be identified [2,11]:

1. bulk gas → gas liquid interface
2. gas liquid interface → bulk liquid
3. bulk liquid → liquid solid interface
4. catalyst pore diffusion and simultaneous chemical reaction.

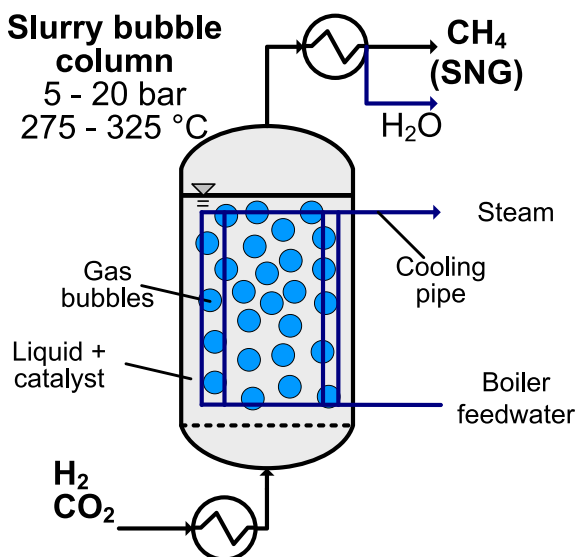


Fig. 1. Schematic of a slurry bubble column reactor for methanation.

In a steady state system, all steps have the same specific flow rate, and the slowest step determines the effective reaction rate  $r_{i,eff}$  (Eq. (5)).

$$r_{i,eff} = -\frac{\dot{n}_{i,G/L}}{V_R} = -\frac{\dot{n}_{i,L/S}}{V_R} = r_{m,i} \cdot \frac{m_{cat}}{V_R} \quad (5)$$

Hence, optimum operating conditions for a SBCR at steady-state can be determined, once the limiting reaction process step is identified. According to the literature and our own estimations, mass transfer within the gas phase (step 1) and from the liquid phase to the catalyst surface (step 3) are not limiting [12,13]. The reaction kinetics (step 4) can be the slowest step at low temperatures (e.g. <250 °C). The limiting step 4 can be described with Eq. (6).

$$r_{i,eff} = r_{m,i} \cdot \frac{m_{cat}}{V_R} = -k_m \cdot \left(\frac{p_i \rho_L}{H_{iL}}\right)^n \cdot \frac{m_{cat}}{V_R} \quad \text{step 4 limiting} \quad (6)$$

However, at high temperatures step 2 is the limiting transfer phenomenon. The step 2 (gas liquid interface → bulk liquid) can be described with Eq. (7) representing the specific molar flow of a gas species  $i$ ,  $\dot{n}_{iL}$ , from the gas/liquid interface to the liquid bulk phase:

$$r_{i,eff} = \frac{\dot{n}_{i,G/L}}{V_R} = (k_L a)_i \cdot (c_{iL}^* - c_{iL}) = (k_L a)_i \cdot \left(\frac{p_i \cdot \rho_L}{H_{iL}} - c_{iL}\right) \quad \text{step 2 limiting} \quad (7)$$

According to Eq. (7) this mass transfer step can be enhanced by increasing:

- the mass transfer coefficient  $k_L$ ;
- the specific gas/liquid interface area  $a = \frac{6\epsilon_G}{d_B}$ ;
- the gas solubility  $c_{iL}^* = \frac{p_i \rho_L}{H_{iL}}$ .

While  $k_L$  and  $a$  are significantly influenced by the system hydrodynamics,  $c_{iL}^*$  depends on the heat transfer liquid and operating conditions (pressure and temperature) [14]. The mass transfer between the gas/liquid interface and the liquid bulk can be notably improved by increasing the gas holdup and by reducing the bubble diameter. The hydrodynamics of a SBCR, and especially the gas holdup  $\epsilon_G$ , is influenced by numerous parameters which can be separated into two categories: reactor geometry (gas distributor, reactor dimensions and fittings) and material properties (gas, liquid and solid phase) [14–16]. The cross sectional area  $A_R$  as well as the height to diameter ratio  $h_R/d_R$  of a SBCR influence the system hydrodynamics in two ways. First, a flow regime change can happen for a fixed gas velocity in a bigger reactor [17–20]. Then, greater backmixing occurs in a bigger reactor because the wall-effects are less important [21].

In this work, experiments have been carried out with a single heat transfer liquid and catalyst (relevant liquid properties are given in Table 2). Accordingly, optimal CO<sub>2</sub> conversion and CH<sub>4</sub> formation rate can be found through variation of the following parameters:

- reactor pressure;
- temperature;
- gas velocity;
- reactor geometry;
- catalyst concentration in the slurry phase;
- H<sub>2</sub> and CO<sub>2</sub> partial pressures.

## 3. Experimental

### 3.1. Experimental setup

The experiments have been carried out using the experimental setup shown in Fig. 2. This setup can be divided into three sections: gas supply, SBCR and gas analytics. The gas supply (CO<sub>2</sub>, H<sub>2</sub>, and Ar as internal standard) was carried out via a set of mass-flow controllers (Bronkhorst). Before going into the SBCR, the feed gas was heated to the desired temperature. At the reactor outlet the product gas was

Download English Version:

<https://daneshyari.com/en/article/209595>

Download Persian Version:

<https://daneshyari.com/article/209595>

[Daneshyari.com](https://daneshyari.com)