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Methanation in a fluidized bed reactor with high initial CO partial pressure: Part II— Modeling and sensitivity study

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ABSTRACT

A model of a bench-scale methanation reactor was set-up by modifying the classical two-phase model approach and introducing an additional bulk flow from bubble to dense phase to consider the volume contraction of the methanation reaction. The model uses experimentally determined kinetics and hydrodynamic correlations from literature. It was satisfyingly validated by comparing the calculated gas concentration profiles with the experimental data, especially with respect to initial reaction rates and reactor exit concentrations.

A sensitivity study with respect to different bubble size correlations, mass transfer rates and considering or neglecting the bulk flow (influence of volume contraction caused by the methanation reaction) was carried out. It showed that the bubble size correlation by Werther and the resulting gas concentration profiles fit the measured data better than the computed gas concentration profiles using the bubble size correlation by Rowe.

Neither a variation of the mass transfer coefficient nor neglecting the bulk flow in the fluidized bed model did yield further improvement of the calculated concentration profiles.

1. Introduction

Fluidized catalyst beds are extensively used in gas–solid applications in which large heat and mass transfer rates are required. The methanation in a fluidized bed with high initial CO partial pressures is an example due to its fast and highly exothermic reaction. Modeling of such a process is, on one hand, advantageous for design purpose as it allows to easily study the influence of the operating conditions. On the other hand, the model requires the knowledge of the hydrodynamics, mass transfer and kinetics. Correlations for hydrodynamic parameters (i.e., bubble growth, bubble velocity, bubble gas hold-up) and for the mass transfer (i.e., mass transfer coefficient, specific mass transfer area) applicable for fluidized bed models are found in the literature. The question arises, how to validate model assumptions and literature based correlations. Data points acquired by spatially resolved gas concentration measurements can be an assist, as model results should not only describe the outlet gas concentration but also the gas concentration profile beginning from the gas distributor till the end of the bed. In Part I of this paper (Kopyscinski et al., 2011), measured profiles in a bench-scale fluidized bed methanation reactor are presented for different experimental conditions. In the present part of this article, a model for a bench-scale reactor is presented in which the calculated gas concentration profiles are compared with the experimental data investigated.

A sensitivity study with respect to different bubble size correlations, mass transfer rates and bulk flows is carried out to better understand the measured phenomena. Moreover, a particle model is used to investigate whether the assumption of absence of pore diffusion limitation inside the catalyst particle holds.

1.1. Previous fluidized bed methanation models

Cobb and Streeter (1979), Bellagi (1979) and Kai et al. (1984) investigated the methanation reaction in a fluidized bed for the production of synthetic natural gas (SNG) by both, experiments and modeling.

During the Bi-Gas project in the 1970s (Streeter, 1977), Cobb and Streeter (Streeter et al., 1976; Cobb and Streeter, 1979) derived from fluidized bed methanation experiments a simple kinetic approach in form of a power law, with first order in CO, $r = kp_{CO}$. The experimental data showed that the mass transfer coefficient was very large. Therefore, the gas was assumed to be totally mixed and the model was reduced to a perfectly mixed reactor. The agreement between calculated and observed conversion of CO at the reactor outlet was satisfactory for such a simple model (within $\pm$ 10%).

In contrary, Bellagi (1979) and Kai et al. (1984) developed a model for the methanation reactor based on the original

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homogenous two-phase fluidized bed model (May, 1959; van Deemter, 1961) with the common assumptions, i.e., isothermal, isobaric, dense phase at minimum fluidization conditions, no particles in the bubble phase, constant bubble phase fraction, constant mass transfer area and thus constant mass transfer coefficient. Both, Bellagi and Kai included an additional convective bulk flow due to the volume contraction in the dense phase, which is inherent to the methanation reaction.

It is not undoubtedly proven yet if such an extra convective bulk flow exists in reality. In Abba et al. (2002) is written that there exists an experimental evidence for the case of volume expansion; it is stated that at least some of the extra gas, which is generated in the dense phase is transported into the bubble phase. But, it is not clear how fast and to what extent the extra mass is transferred. Little work has been done on this subject for both volume expansion and reduction (Abba et al., 2002; Sitzmann, 1986; Böck, 1984; Irani et al., 1980; Kai and Furusaki, 1984; Kai and Furusaki, 1987; Shiau and Lin, 1993; Tafreshi et al., 2000; Kai et al., 2006).

In his simulation of the methanation, Bellagi neglected the water gas shift reaction and investigated the influence of the dense phase flow (mixed, plug flow), the kinetics (linear, non-linear) and the convective bulk flow. The kinetics were expressed by a simple power law in linear and non-linear form as $r = kp_{H_2}$ and $r = kp_{CO}^{-0.31}p_{H_2}^{0.85}$, respectively. The exponents of the non-linear form were derived from the same fluidized bed experiments. The results of the predicted and experimentally determined values for the CO conversion versus temperature are shown in Fig. 1. The models assuming a completely mixed dense phase show a better agreement with the experimental data than the models assuming plug flow in both phases, Fig. 1a. Furthermore, the models containing the non-linear kinetics could not describe the experimental data. Bellagi assumed that the reaction orders are too small. Moreover, he presumed a reaction order of H_2 closer to one and for CO closer to zero, so that the overall order of reaction is about one (Bellagi, 1979).

In addition to Bellagi's model, Kai et al., 1984) implemented a Langmuir–Hinshelwood rate expression for the methanation reaction determined in a fixed bed reactor system. Furthermore, Kai included the water gas shift reaction and treated the average bubble diameter as an adjustable parameter. By minimization of the deviation of the calculated and measured CH_4 and CO_2 yields, the average bubble diameter was found to be 3.6 cm. This bubble size corresponds to almost 50% of the bed diameter.

Kai et al. investigated the CO-methanation in a fluidized bed reactor at 300 °C and 1 bar, with a superficial gas velocity of $u = 0.1 - 0.3\ \mathrm{m\ s^{-1}}$, and molar ratio of $H_2/CO = 1.7 - 3.2$.

Kai stated as well that a fluidized bed model, which does not consider the decrease of moles and thus the extra mass transfer, cannot describe the measured data (Kai et al., 1984) while his model taking the volume contraction into account, predicted the outlet conversion of the reactor within ±10%.

2. Modeling approach

There exists a variety of fluidized bed models with different complexities. In this, work a simple homogeneous two-phase model is chosen. No cloud and wake phase is considered and by this only one interchange mass transfer coefficient is required. The presented model is based on the two-phase fluidized bed model (May, 1959; van Deemter, 1961), to which several improvements were added to account for different assumptions, e.g. that the volume contraction in the dense phase due to the methanation reaction is always immediately balanced out by an additional so-called "convective" mass transfer from the bubble phase to the dense phase. Further details are described in Kopyscinski et al. (in press). This one-dimensional model allows the comparison of predicted and measured dense phase concentration profiles for validation.

The mass balance for the bubble and dense phase are described in Eqs. (1) and (2), respectively

$$0 = -\frac{d\dot{n}_{b,i}}{dh} - K_{G,i}aA(c_{b,i} - c_{e,i}) - \dot{N}_{vc}x_{b,i} \tag{1}$$

$$0 = -\frac{d\dot{n}_{e,i}}{dh} + K_{G,i}aA(c_{b,i} - c_{e,i}) + \dot{N}_{vc}x_{b,i} + (1-\varepsilon_b)(1-\varepsilon_{mf})\rho_P AR_i$$

$$\underbrace{\frac{\mathrm{mol}}{\mathrm{m\,s}}}_{\text{convection}} + \underbrace{\frac{\mathrm{m}}{\mathrm{s}}\frac{1}{\mathrm{m}}\mathrm{m}^2\frac{\mathrm{mol}}{\mathrm{m}^3_{\mathrm{bed}}}}_{\text{mass transfer}} + \underbrace{\frac{\mathrm{mol}}{\mathrm{m\,s}}}_{\text{bulk flow}} + \underbrace{\frac{\mathrm{m}^3_{\mathrm{dense}}}{\mathrm{m}^3_{\mathrm{bed}}}\frac{\mathrm{m}^3_{\mathrm{solid}}}{\mathrm{m}^3_{\mathrm{dense}}}\frac{\mathrm{kg_{cat}}}{\mathrm{m}^3_{\mathrm{solid}}}\mathrm{m}^2\frac{\mathrm{mol}}{\mathrm{s\,kg_{cat}}}}_{\text{reaction}} \tag{2}$$

Here, a is the specific mass transfer area, A is the cross sectional area of the reactor, $K_{G,i}$ is the mass transfer coefficient, $x_{b,i}$ is the molar fraction in the bubble phase, ρ_P is the particle density, $(1-\varepsilon_b)$ is the volume fraction of the dense phase and $(1-\varepsilon_{mf})$ is the volume fraction of the particles. The reaction term includes the rate equations and kinetic parameters determined previously by Kopyscinski et al. (Kopyscinski et al., 2010a; Kopyscinski et al., 2010b).

The total bulk flow from the bubble to the dense phase $\dot{N}_{vc}$ is described as the sum of the molar losses due to the reaction and

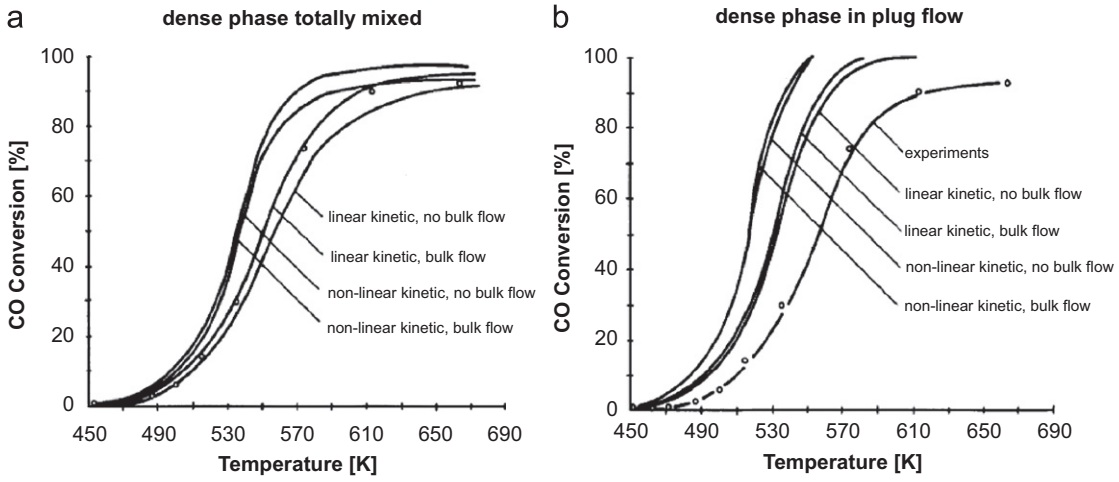

Fig. 1. CO conversion as a function of temperature for the different models. (a) Models with plug flow in bubble and complete mixed in dense phase and (b) models with plug flow in both phases, adapted from Bellagi and Hammer (1984).