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Fischer–Tropsch synthesis in milli-structured fixed-bed reactors: Experimental study and scale-up considerations

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ABSTRACT

The low-temperature Fischer–Tropsch synthesis (FTS) over a CoRe/γ-Al_2O_3 catalyst in milli-structured fixed-bed reactors was studied experimentally and theoretically. Kinetic and pressure drop measurements were conducted in a capillary with a catalyst bed length of 1 m. Ergun constants for calculation of the pressure drop were determined by measurements in the absence of reaction. Kinetic constants for the assumed first-order kinetics were obtained with the aid of a reactor model taking into account the volume contraction during reaction as well as the pressure drop. With the same model, values for the liquid holdup in the reactor were estimated. Finally, simulations for a scale-up of the reactor were conducted. It could be shown that effective heat removal is possible even for reaction channel widths of 1.5 mm and 3 mm. Catalyst particle sizes of 100 μm, 200 μm and 350 μm allow for high effectiveness factors at acceptable pressure drops. High catalyst and reactor volume specific productivities can be obtained resulting in compact and efficient reactors. In conclusion, milli-structured fixed-bed reactors appear to be an interesting concept especially for small-scale FTS units.

1. Introduction

In face of decreasing global oil reserves there is a strong need for alternative sources fulfilling the growing demand for liquid fuels. The Fischer–Tropsch synthesis, which was developed in the 1920s, offers the possibility of producing liquid hydrocarbons from synthesis gas as base for synthetic fuels. During this highly exothermic polymerization-like reaction of CO and H_2 hydrocarbon chains are formed with H_2O as by-product. In the modern low-temperature Fischer–Tropsch (FT) process liquid products are formed from the gaseous educts at temperatures between 473 K and 523 K under elevated pressure. Two reactor types are used on commercial scale, the slurry bubble column and the tubular fixed-bed reactor. Main disadvantage of the slurry bubble column is the highly elaborate separation of the fine catalyst particles from the liquid product whereas the tubular fixed-bed reactor mainly suffers from insufficient heat removal [1]. Micro- and milli-structured reactors allow for a strong increase of heat transport in radial direction and thus isothermal operation even of highly exothermic reactions becomes feasible [2]. The term milli-structured refers to structures larger than 1000 μm.

A solid catalyst can be placed in a structured reactor by coating the walls or by using a fixed-bed of sufficiently small catalyst particles. Klemm et al. [3] have postulated that the fixed-bed concept for reasons of relatively high pressure drop and less efficient radial heat transfer in comparison to wall coated structures is feasible for research reactors and small scale production units only. On the other hand, the fixed-bed arrangement has several major advantages such as the possibility to use industrially proven catalysts, easy exchange of spent catalysts [4] and much higher catalyst inventory than in wall reactors [5]. Velocys Inc. have already tested milli-structured fixed-bed reactors for FTS and obtained very promising results. Cao et al. [6] have reported successful experiments in a multichannel fixed-bed micro-reactor for simultaneous screening of FT catalyst as an instrument for faster catalyst development. Jarosch et al. [7] conducted experiments with a Co:Re (21:1) catalyst on γ-Al_2O_3 with particle sizes in the range of 177–250 μm in a catalyst bed of approx. 3 cm length. Operated at 41 bar and 523 K, a maximal catalyst productivity of 1700 kg m_{cat}^{-3} h^{-1} was achieved. Based on these results, scale-up calculations for a 30,000 bbl d^{-1} plant based on microchannel technology were carried out. Recently, Myrstad et al. [8] also described experiments in a multichannel micro-structured reactor with γ-Al_2O_3 based catalysts, consisting of Co:Re (20:0.5 and 40:1) and particle sizes in the range of 53–90 μm. The measurements were carried out in a cross-flow oil heated micro-reactor of 800 μm channel height with a catalyst mass of 1.5 g. The obtained results revealed better mass and heat transfer properties of the micro-reactor as a conventional lab-scale fixed-bed reactor. Under typical FTS conditions the pressure drop did not exceed 1.5 bar m^{-1} at operating pressures of 20 bar and 30 bar, respectively.

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In the present contribution results of an experimental and modeling study of milli-structured fixed-bed reactors for FTS are presented. Measurements were conducted with sieve fractions of a Re promoted Co/γ-Al_2O_3 catalyst in a capillary reactor. Special emphasis was placed on pressure drop measurements with and without reaction. Based on the experimental results, a mathematical model for a structured fixed-bed reactor was developed. The potential of milli-structured fixed-bed FTS reactors was evaluated in a scale-up study assuming a small-scale unit with a production capacity of 500 bbl d^{-1}.

2. Experimental

2.1. Catalytic measurements

The catalyst used in this study consisted of approx. 19 wt.% Co and 1 wt.% Re on γ-Al_2O_3 and was prepared as described elsewhere [9]. Reaction rate measurements were carried out with a catalyst sieve fraction of 140–200 μm. The 1/8 in. capillary reactor with 1.753 mm inner diameter had a preheating zone of 0.5 m length and a catalyst packing height of 1.0 m. A packing porosity of 0.335 was calculated from the measured apparent density of the catalyst particles. After heating in N_2 with 1 K min^{-1} the catalyst was reduced for 36 h under a flow of 10% H_2 in N_2 at atmospheric pressure and a temperature of 623 K and then cooled down to room temperature in pure N_2 again. The capillary reactor was then transferred to a heating circulator (Julabo SL-6) in a continuously operated experimental setup (Fig. 1). After mounting the capillary reactor, the setup was purged with N_2 and afterwards pressurized with synthesis gas using a backpressure regulator (Tescom 44-1700). The gaseous educts H_2 and CO with a ratio of 2:1 as well as the internal standard Ar were fed to the setup by mass flow controllers (Bronkhorst El-Flow F-230M). The pressure drop was measured between the inlet and outlet of the capillary reactor with a differential pressure transmitter (Endress+Hauser, Deltabar S PMD 75). Downstream the capillary reactor the products were transferred in a heated tube to a wax and water separator operated at 423 K and 273 K, respectively. A gas stream of 2 mL min^{-1} leaving the water separator was fed to a Varian CP-3800 GC for online gas analysis. The GC was equipped with a TCD and a FID channel for analyzing permanent gases and gaseous hydrocarbons, respectively. The TCD channel consisted of a sample loop (1 mL) and three packed columns (2 × Hayesep Q 80/100 0.5 m × 1/8 in., Molsieve-13X 80/100 1.5 m × 1/8 in.). The FID channel consisted of a sample loop (250 μL) and a CP-Sil 5 CB column (60 m × 0.25 mm × 1 μm). The CO conversion X_{CO} and the methane selectivity S_{CH_4} were calculated with Eqs. (1) and (2), where R is the peak area ratio of species CO or CH_4 and the internal standard and f a specific calibration factor.

$$X_{CO} = \frac{R_{CO,in} - R_{CO}}{R_{CO,in}} \quad (1)$$

$$S_{CH_4} = f \frac{R_{CH_4}}{R_{CO,in} - R_{CO}} \quad (2)$$

Offline analysis of the liquid product was conducted in a HP 5890 Series II Plus GC with an Agilent J&W DB-2887 column using simulated destillation according to the ASTM D 2887 method. The chain growth propability α was calculated from the results for the C_{15} to C_{25} species. The catalyst was activated for each 24 h at 433 K and 443 K under synthesis gas before increasing the temperature further and starting the catalytic measurements.

2.2. Measurement and evaluation of pressure drop

The pressure drop in fixed-beds comprises frictional (viscous term) and inertia (kinetic term) effects, which are characterized by a linear and quadratic dependence on the flow velocity, respectively. These effects are described by the Ergun equation (Eq. (6)), which was developed for infinitely extended beds and spherical particles with uniform size distribution. However, it can be modified for other cases by determining specific Ergun constants [10].

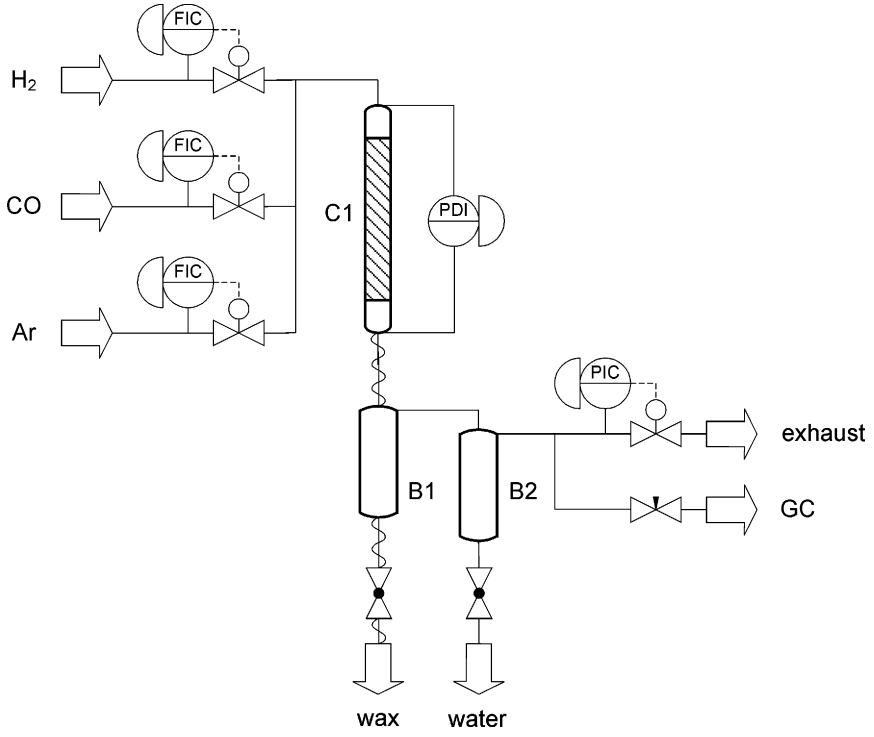

Fig. 1. Schematic of the experimental setup (C1: capillary reactor, B1: hot separator, B2: cold separator).