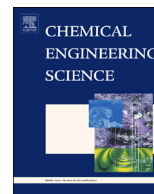




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# Laboratory and pilot plant fixed-bed reactors for Fischer–Tropsch synthesis: Mathematical modeling and experimental investigation



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## HIGHLIGHTS

- Reactors for Fischer–Tropsch synthesis are studied in laboratory and pilot plant.
- A two-dimensional mathematical model for fixed-bed reactor is proposed.
- The validity of the model is tested over a wide range of operating conditions.
- The effects of major process parameters on the reactor performance are revealed.

## ARTICLE INFO

## Article history:

Received 22 January 2015

Received in revised form

22 June 2015

Accepted 29 July 2015

Available online 10 August 2015

## Keywords:

Fischer–Tropsch synthesis

Fixed-bed reactor

Mathematical modeling

Experimental investigation

## ABSTRACT

The present work describes the development of a comprehensive two-dimensional heterogeneous model of a fixed-bed reactor for Fischer–Tropsch synthesis. The chemical kinetics for cobalt-based catalysts is modeled on the basis of the LHHW approach. The intraparticle transport model takes into account the fact that the catalyst pores are filled with liquid hydrocarbons and water due to capillary condensation under realistic conditions. The validity of the reactor model is tested against the experimental data from laboratory and pilot plant fixed-bed reactors over a wide range of operating conditions. Detailed numerical simulations are performed to investigate the effect of major process parameters on the reactor performance.

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## 1. Introduction

Fischer–Tropsch synthesis (FTS) is the most common major second stage of gas-to-liquids (GTL) technology. FTS is responsible for conversion of synthesis gas (carbon monoxide and hydrogen mixture) into a mixture of linear hydrocarbons. Since both capital and operational costs of GTL are limited by the mature syngas production stage (Dry, 1996), any further efficiency optimization can be achieved by maximizing the FTS syngas conversion and hence carbon efficiency of a whole GTL (Dry, 1999). The high conversion performance may be realized through active catalysts, which are numerous in the literature, and a proper catalytic reactor.

Fischer–Tropsch synthesis is a highly exothermic multiphase catalytic process with overall reaction enthalpy of about 170 kJ/mol. More advanced low temperature FTS is carried out in a temperature range between 200 and 250 °C under high pressure between 20 and 50 bar in multitubular fixed-bed or slurry bubble column reactors (Dry, 1999; Guettel et al., 2008; Guettel and Turek, 2009). Due to a wide range of products the pores of the catalysts are often filled with liquid hydrocarbons and water (Madon and Iglesia, 1994). Accumulation of liquids decreases CO and H<sub>2</sub> transport to active sites of the catalysts.

The drive to more efficient industrial scale realization of Fischer–Tropsch process may be accomplished through application of various catalytic systems and different reactor types as witnessed by numerous literature sources. Every reactor design type, such as slurry-phase, or microchannel, or fluidized-bed, or fixed-bed, requires its own approach in modeling and optimization (Dry, 1999; Guettel et al., 2008; Guettel and Turek, 2009). This work is devoted to the problem of a tubular fixed-bed reactors

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with cobalt-based catalysts, since this case is the most common in practice and, in particular, is a subject of many researches in our group.

Multitubular fixed-bed reactors are the most well-known reactors that make it possible to achieve high CO conversion and liquid products selectivity (Sie and Krishna, 1998). But it has several drawbacks such as relatively high pressure drop, tube diameter restrictions, intraparticle diffusion limitations (Sie and Krishna, 1999). These facts result in complexity of kinetics and transport restrictions in Fischer–Tropsch synthesis and complicate direct scale-up of the reactor. In this case mathematical modeling is the method of reducing the development time and material losses.

## 2. Experimental investigation

The pilot plant created in close cooperation with Technological Institute for Superhard and Novel Carbon Materials and INFRA Technology (see Fig. 1) allows testing of the Fischer–Tropsch process in different single-tube and multi-tubular reactors proposed for use in serial industrial-scale units. The reactor is designed as a fixed-bed of pelletized Cobalt-based catalyst. Tube length varies from 1.5 m to 6 m long. The pilot runs have confirmed the process productivity in excess of 300 kg of liquid hydrocarbons per one cubic meter of the catalyst per hour and produced samples of liquid hydrocarbons for commercial testing.

A principal process flow diagram of the Fischer–Tropsch synthesis unit is shown in Fig. 2. Synthesis gas (molar ratio  $H_2/CO = 2$ , pressure 20 bar) is fed to FTS reactor (1) at room temperature. The gas and liquid products and unconverted synthesis gas are directed to the heat exchanger (4) and cooled down by water. Gas phase and liquid phase are separated in the separator (2). Liquid phase flows to the next separator (3), where the liquid phase is separated into syncrude and water. The gaseous product is purged, while a small part of it is taken for chromatographic analysis.

Experimental investigation was done in the single-tube reactor shown in Fig. 3. The catalytic bed is not shown in this figure. The total height of the half-inch tube is 2.1 m. The synthesis gas is fed through the inlet (3) of the tube (2), where it is first heated in the inert bed, then passes through the catalytic bed. The Fischer–Tropsch product (unconverted synthesis gas along with liquid products) is removed from the bottom of the reactor tube (4). Catalytic bed temperature is measured by 10 thermocouples (7). It allows to monitor the temperature profile along the reactor. The synthesis temperature is maintained by circulation of pressurized water in the reactor jacket. Water is heated in the feed water heater before moving into reactor jacket (1). The pump circulates the water through the piping (5) and (6). The circulating water provides very efficient heat removal.

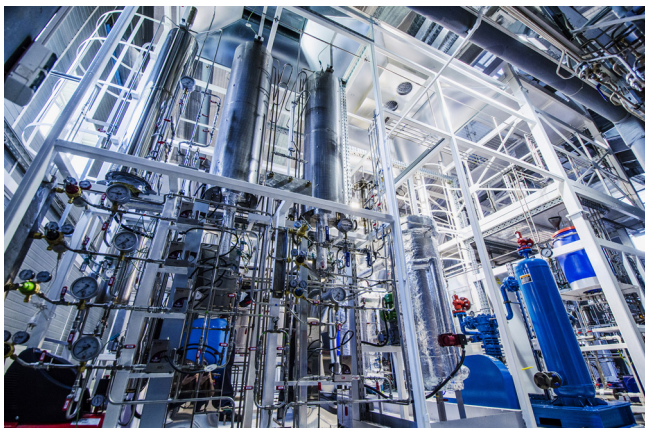


Fig. 1. Pilot plant.

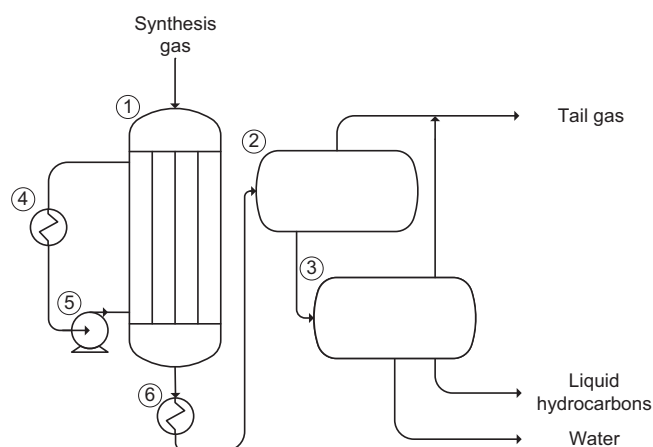


Fig. 2. Principal process flow diagram of the Fischer–Tropsch synthesis unit. 1 – catalytic reactor, 2 – gas–liquid separator; 3 – liquid product separator, 4, 6 – heat exchangers; 5 – circulation pump.

Indeed, as soon as the water temperature exceeds boiling point at the given pressure, the flow becomes two-phase (vapor–liquid) and the heat removal efficiency increases greatly. Thermocouples (8) and (9) measure water flow temperature at the top and the bottom of the reactor jacket, respectively.

In this work we use catalysts described in Mordkovich et al. (2012). The bulk density of the granulated catalysts with a diameter of 2.5 mm and length of 3.5 mm is  $1 \text{ g/cm}^3$ . The heat capacity and thermal conductivity of the catalysts are  $1.0 \text{ kJ}/(\text{kg} \cdot \text{K})$  and  $3.5 \text{ W}/(\text{m} \cdot \text{K})$  respectively. The voidage of the fixed-bed is 0.6. The porosity and tortuosity of the granules are taken to be 0.7 and 3.0 respectively.

The experimental investigation was preceded by the catalyst activation in hydrogen at temperature  $400 \text{ }^\circ\text{C}$  and pressure 1.2 bar. The activation procedure is described in details in Sineva et al. (2014).

After the activation procedure the reactor was heated introducing of synthesis gas, raising the temperature from  $170 \text{ }^\circ\text{C}$  to  $230\text{--}240 \text{ }^\circ\text{C}$  by  $3\text{--}10 \text{ }^\circ\text{C}$  steps every 6 h. Synthesis gas pressure was 20 bar. Synthesis gas (molar ratio of  $H_2/CO = 2$  with 5 vol% of  $N_2$  as internal reference) was supplied at gas-hour space velocity (GHSV) of  $1000 \text{ h}^{-1}$  while the temperature was raised to the optimal value and then GHSV was increased stepwise up to  $5000 \text{ h}^{-1}$  to optimize the productivity. The temperature was optimized for every GHSV thus maximizing productivity.

Composition of both gas and liquid products was determined chromatographically. Analysis of the feed mixture and gaseous products ( $CH_4$ ,  $CO_2$ ,  $C_2\text{--}C_4$  hydrocarbons) was done by gas absorption chromatography (thermal conductivity detector, carrier gas – helium, gas flow rate  $20 \text{ ml/min}$ ). A column with molecular sieves CaA ( $3 \text{ m} \times 3 \text{ mm}$ ) was used for the separation of CO and  $CH_4$ . The HayeSep column ( $3 \text{ m} \times 3 \text{ mm}$ ) was used for the separation of  $CO_2$  and  $C_2\text{--}C_4$  hydrocarbons. The temperature-programming mode used ( $60\text{--}200 \text{ }^\circ\text{C}$ ,  $10 \text{ }^\circ\text{C/min}$ ).

Composition of liquid products was determined by gas–liquid chromatography (flame ionization detector, carrier gas – helium, gas flow rate  $30 \text{ ml/min}$ ). The 50 m long capillary column with DP-Petro plate was used.

## 3. Mathematical modeling

### 3.1. Mass balance in gas phase

The continuity equation or the mass balance equation ensures that the overall change of mass within a continuum is zero. The equation for conservation of mass for a free flow region is as

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