



Fischer–Tropsch synthesis product selectivity over an industrial iron-based catalyst: Effect of process conditions

Branislav Todic^{a,b}, Lech Nowicki^c, Nikola Nikacevic^b, Dragomir B. Bukur^{a,d,*}

^a Chemical Engineering Program, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar

^b Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia

^c Lodz University of Technology, Faculty of Process and Environmental Engineering, Wolczanska 213, 90-924 Lodz, Poland

^d Texas A&M University, 3122 TAMU, College Station, TX 77843, United States

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ABSTRACT

The effect of process conditions on product selectivity of Fischer–Tropsch synthesis (FTS) over industrial iron-based catalyst (100 Fe/5 Cu/4.2 K/25 SiO₂) was studied in a 1-L stirred tank slurry reactor. Experiments were performed over a range of different reaction conditions, including three temperatures ($T=493$, 513 and 533 K), four pressures ($P=0.8$, 1.5, 2.25 and 2.5 MPa), two synthesis gas feed molar ratios ($H_2/CO=0.67$ and 2) and gas space velocity from 0.52 to 23.5 Ndm³/g-Fe/h. The effect of process conditions on reaction pathways of FTS and secondary 1-olefin reactions was analyzed by comparing product selectivities, chain growth probabilities and ratios of main products (n-paraffin, 1- and 2-olefin). Reduction of methane production and increase of C₅₊ products was achieved by decreasing temperature, inlet H₂/CO ratio and/or increasing pressure. Overall selectivity toward methane and C₅₊ did not show significant changes with variations in residence time. All of the product selectivity variations were shown to be related to changes in chain length dependent growth probabilities.

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1. Introduction

Natural resources, such as coal, natural gas and biomass, can be converted into liquid hydrocarbon fuels via the Fischer–Tropsch synthesis (FTS) reaction. FTS is a heterogeneous reaction first discovered in the early twentieth century [1]. Reactants, carbon monoxide and hydrogen, are converted to an array of long chain molecules, mainly consisting of n-paraffins and 1- and 2-olefins:



The main advantage of such synthetic fuel mixtures is their purity compared to conventional oil-derived fuels, since they do not contain nitrogen, sulfur nor aromatic compounds. These environmental, as well as economic, reasons have led to the intensification of research into FTS technology during the last two decades.

The catalysts of choice for industrial FTS are cobalt and iron. If the raw material is coal, then the preferred catalyst is usually

iron [2,3]. One of the main features of iron FTS catalysts is their water-gas-shift (WGS) activity. WGS reaction can be presented as:



The WGS reaction provides additional hydrogen for FTS, which is needed in the case of coal-derived syngas. Coal-derived syngas has a H₂/CO ratio below 2, the latter being an approximate stoichiometric H₂/CO ratio needed to produce hydrocarbons according to Eqs. (1) and (2).

The exact sequence of elementary steps in FTS is still under debate [4,5]. It is, however, generally accepted that FTS follows a polymerization type mechanism. The products can be described by the Anderson–Schulz–Flory (ASF) model [6], where the molecular mass distribution is governed by a chain growth probability factor (α). The ASF model typically provides a good description of the product distribution in the low carbon range (below C₁₀), while the higher carbon number products deviate and are present in an amount higher than predicted by the ASF distribution model. This is because α does not have a constant value, but in fact increases with carbon number from C₃ before reaching an asymptotic value at higher carbon number range (typically above C₁₅) [7]. Typical deviations from the ASF distribution include higher methane and lower C₂ [8,9]. Another important feature of FTS products is the ratio between various main products (n-paraffin/1-olefin and

* Corresponding author at: Texas A&M University, 3122 TAMU, College Station, TX 77843, United States.

E-mail address: dragomir.bukur@qatar.tamu.edu (D.B. Bukur).

2-olefin/total olefin). The 1-olefin/n-paraffin ratio decreases exponentially for C_3+ hydrocarbons, whereas the amount of 2-olefin in total olefin of the same carbon number increases with carbon number. Ratios of hydrocarbon products are particularly important in studies of the 1-olefin secondary reactions (e.g. hydrogenation to n-paraffin, isomerization to 2-olefin, readsorption and continued chain growth [10–12]).

The delicate interplay between the kinetics of various parallel reactions (FTS, WGS and olefin secondary reactions), at different process conditions, determines the overall selectivity of FTS products. One of the main goals in FTS is to achieve high selectivity of desired C_{5+} products and reduce methane selectivity. Proper selection of process conditions is important in achieving this goal. Even though there is number of studies and reviews describing how variation of each process parameter (temperature, pressure, reactant feed ratio and conversion level) affects overall FTS selectivity [8,13–18], the understanding of reasons for the observed behaviors is still incomplete. Catalyst composition, in particular its potassium content, plays a crucial role in determining the FTS product distribution and how it changes with process conditions [15,16,19–21].

Here we present results from experiments in a stirred tank slurry reactor obtained over a wide range of process conditions using Ruhrchemie catalyst (Fe/Cu/K/SiO₂), and analyze the effect of process conditions on hydrocarbon product distribution, chain growth probability, oxygenates and olefin selectivities. This is an extension of our work with the Ruhrchemie catalyst [14] both in terms of the range of process conditions employed and data analysis. Based on these results, some qualitative conclusions are drawn about reaction pathways and kinetics of primary FTS reactions, and secondary 1-olefin reactions.

This paper is dedicated to Professor Bartholomew who has made significant contributions to advancement of our knowledge about various aspects of FTS [22–26].

2. Experimental

2.1. Catalyst preparation and activation

Commercial precipitated iron FTS catalyst obtained from Ruhrchemie AG (Oberhausen-Holtent, Germany) was used in this study. This catalyst (designated as LP 33/81) was used initially in fixed-bed reactors at Sasol in South Africa and its preparation procedure was described by Frohning et al. [27]. Its nominal composition is 100 Fe/5 Cu/4.2 K/25 SiO₂ (in parts by weight). The catalyst (11–25 g) was calcined in air at 300 °C and a sample with a size fraction between 140 and 325 mesh (44–105 μm) was loaded into the reactor filled with 300–320 g of Durasyn 164 oil (a hydrogenated 1-decene homopolymer, ~C₃₀ obtained from Albermarle Co.). The catalyst was pretreated in CO at 280 °C, 0.8 MPa, and 3 NL/g-cat/h (where, NL/h, denotes volumetric gas flow rate at 0 °C and 1 bar) for 12 h.

2.2. Reactor system and operating procedures

Three tests (runs 1, 2 and 3) were conducted in a 1 dm³ stirred tank slurry reactor (Autoclave Engineers). Schematic of slurry reactor system is shown in Fig. 1. The feed gas flow rate was adjusted with a mass flow controller and passed through a series of oxygen removal, alumina and activated charcoal traps to remove trace impurities. In the present study a premixed synthesis gas mixtures of desired H₂/CO ratios were used. After leaving the reactor, the exit gas passed through a series of high and low (ambient) pressure traps to condense liquid products. High molecular weight hydrocarbons (wax), withdrawn from a slurry reactor through a porous cylindrical sintered metal filter, and liquid products, collected in

the high and low pressure traps, were analyzed by capillary gas chromatography. Liquid products collected in the high and atmospheric pressure traps were first separated into an organic phase and an aqueous phase and then analyzed using different columns and temperature programmed methods. The reactants and non-condensable products leaving the ice traps were analyzed on an on-line GC (Carle AGC 400) with multiple columns using both flame ionization and thermal conductivity detectors. Stirring speed of 1200 rpm was used to minimize external mass transfer resistance. Further details on the experimental set up, operating procedures and product quantification can be found elsewhere [14,28].

After the pretreatment the catalyst was tested initially at 260 °C, 1.5 MPa, 4 NL/g-Fe/h using CO rich synthesis gas (H₂/CO molar feed ratio of 0.67). After approaching a steady state (~60 h on stream) the catalyst was tested at different process conditions (total of 25 sets of process conditions in three tests/runs). The minimum length of time between changes in process conditions was 20 h.

2.3. Experimental data

In total 25 sets of data at different process conditions were obtained in three separate runs (with two replicates of baseline process conditions), involving 12, 7 and 8 mass balances, respectively. The conditions and selected results are summarized in Table 1. Data were obtained at three reaction temperatures ($T=493, 513$ and 533 K), four pressures ($P=0.8, 1.5, 2.25$ and 2.5 MPa), and two synthesis gas feed molar ratios (H₂/CO = 0.67 representative of coal derived synthesis gas and H₂/CO = 2 representative of syn-gas from natural gas). The gas space velocity (SV) was varied from 0.52 to 23.5 Ndm³/g-Fe/h to obtain a wide range of conversions ($X_{CO}=9\text{--}84\%$).

Following formulas were used to calculate conversions and selectivities:

- CO conversion (% by moles)

$$X_{CO} = 100\% \times \frac{(\text{Moles of CO at inlet}) - (\text{Moles of CO at outlet})}{(\text{Moles of CO at inlet})} \quad (4)$$

- CO₂ selectivity (% by moles)

$$S_{CO_2} = 100\% \times \frac{\text{Moles of CO}_2 \text{ at outlet}}{(\text{Moles of CO at inlet}) - (\text{Moles of CO at outlet})} \quad (5)$$

- C_n selectivity (% by mass in hydrocarbons)

$$S_{C_n} = 100\% \times \frac{\dot{m}_{C_n}}{\dot{m}_{HC, total}} \quad (6)$$

where \dot{m}_{C_n} is the mass flowrate of hydrocarbons with n carbon atoms.

- C₅₊ selectivity (% by mass in hydrocarbons)

$$S_{C_{5+}} = 100\% - \sum_{n=1}^4 S_{C_n} \quad (7)$$

- Selectivity can also be expressed in C-atom % basis, which is especially useful when only gas phase analysis is performed (i.e. no liquid samples are collected).

$$S_{C_n} = 100\% \times \frac{n \times \text{Moles of C}_n \text{ at outlet}}{(\text{Moles of CO at inlet}) - (\text{Moles of CO at outlet}) - (\text{Moles of CO}_2 \text{ at outlet})} \quad (8)$$

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