



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Effects of experimental operations on the Fischer-Tropsch product distribution

Ruyi Yang^{a,c}, Liping Zhou^{b,*}, Junhu Gao^b, Xu Hao^{a,b}, Baoshan Wu^{a,b,*}, Yong Yang^{a,b}, Yongwang Li^{a,b}

^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China

^b National Energy Center for Coal to Liquids, Synfuels China Co., Ltd., Huairou District, Beijing 101400, PR China

^c University of Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

Keywords:

Fischer-Tropsch synthesis
Simulated distillation
Product distribution
Flash loss
Separation

ABSTRACT

The present study provides insight into the effect of experimental operations on the Fischer-Tropsch synthesis (FTS) product distribution by combining experimental and theoretical analyses of the process. Experimental errors originated from GC data processing and product collecting conditions are addressed here based on the experimental data obtained using commercial iron-based catalyst in a tubular fixed-bed reactor. A corrected area normalization method, which is a combination of the area normalization and simulated distillation, is proved to be an accurate and convenient method for FTS heavy oil chromatogram quantification. The flash loss from the hot trap and the cold trap is found to be negligible under the normal operating conditions. However, water may be condensed remarkably in the hot trap at low temperature and wrapped by wax. In addition, the selectivity of the high-carbon-number alcohols will be seriously underestimated at low temperature of the hot trap. The FTS product distributions under a wide range of reaction conditions are exhibited.

1. Introduction

Fischer-Tropsch Synthesis which converts carbonaceous materials such as coal, renewable biomass, and natural gas (via gasification) into clean transport fuels or other valuable organics has received great attention in the past decades [1,2]. Generally speaking, FTS is a polymerization-like reaction and the product spectrum consists of a very broad range of hydrocarbons (mainly linear paraffin and linear olefin) and oxygenates (mainly alcohol), with carbon number from C₁ to even C₁₂₀₊. The Anderson-Schulz-Flory equation is usually introduced to describe the relative ratios of these polymers of different length, with one constant chain growth probability, regarded as ASF distribution. However, a straight line of the hydrocarbon distribution only occurs when the process produce light hydrocarbons, e.g. carbon number below fourteen. Tremendous experimental results showed that the hydrocarbon selectivity did not obey the ideal ASF distribution under the industrial operating conditions [3–13]. The compositions decrease gradually with the increasing carbon number but show some irregularities at the same time, as exhibited in Fig. 1. The main trend is approximately fitted by a so-called double- α (α_1 and α_2) distribution [14–17]. Besides, some worse irregularities deviating from the double- α distribution occurred [4–9]. Case 1 and case 4 are some saddle-like

shapes that appeared around C₁₀–C₂₅ and heavier hydrocarbons, respectively, depending on the specific catalysts and the experimental conditions. Case 2 and Case 3 refer to some positive and negative deviations at high-carbon-number region.

The cause of these deviations is a truly controversial issue. Lots of studies tried to explain it by the olefin re-adsorption and the subsequent secondary reactions, by the promoters' effects on the FTS catalysts which may lead to different kinds of active sites, or by the existence of multiple reaction mechanisms in the chain growth process [16,18]. Some others even attributed it to the cracking of heavier hydrocarbons which may happen under the FTS reaction conditions because of the acid-supported catalysts [7]. Our recent studies showed that the experimental artifacts in FTS data collection also played a very important role in the patterns of the product distribution curve. Considering the importance of the FTS experimental data to the reaction mechanism assumption, the product kinetic modeling and even the catalyst development and selectivity control, the present article further clarifies the influence of the experimental artifacts on the FTS product distribution, e.g., the product analysis methods, the product condensing and collecting and flash loss, based on the experimental results and the theoretical calculation.

* Corresponding authors at: National Energy Center for Coal to Liquids, Synfuels China Co., Ltd., Huairou District, Beijing 101400, PR China.

E-mail addresses: zhouliping@synfuelschina.com.cn (L. Zhou), wbs@sxicc.ac.cn, wubaoshan@synfuelschina.com.cn (B. Wu).

<http://dx.doi.org/10.1016/j.cattod.2017.05.056>

Received 30 September 2016; Received in revised form 22 March 2017; Accepted 15 May 2017

0920-5861/ © 2017 Elsevier B.V. All rights reserved.

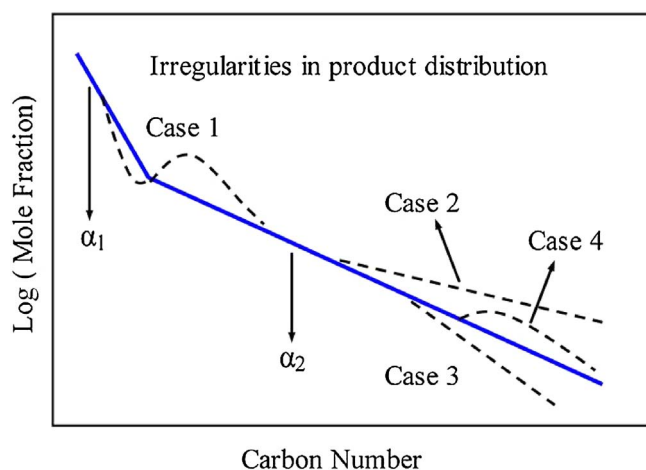


Fig. 1. The commonly appeared irregularities in the FTS product distribution. The solid line: approximately estimating of FTS product distribution by a double- α model; the dashed lines: case 1 and case 4 are some saddle-like shapes that appeared around C10-C25 and heavier hydrocarbons, respectively. Case 2 and Case 3 are some positive and negative deviations at high-carbon-number region. (Reprinted from Industrial & Engineering Chemistry Research, 51 (2012) 11618–11628.) [28].

2. Experimental

2.1. Catalyst and reduction

The industrial iron-based catalysts were provided by Synfuels China Co., Ltd. Typically 1.0 g catalyst with particle size 150–180 μm was used in order to eliminate the internal diffusion. Prior to its use, the catalysts were reduced by synthesis gas at $\text{H}_2/\text{CO} = 2$, $T = 260^\circ\text{C}$, $P = 0.1\text{ MPa}$, space velocity (s.v.) = $1000\text{ mL g}^{-1}\text{ h}^{-1}$ for 48 h. The detailed characterization and properties of the catalysts could be seen elsewhere [19].

2.2. Experimental setup

In view of the close relationship between the experimental setup and the accuracy of the experimental data, the reactor to be used in product distribution study should be considered carefully. Several types of reactors have been used in bench-scale FTS experimental data collection in published papers, e.g., stirred slurry autoclave, spinning basket reactor, Berty-type internal recycle reactor and tubular fixed-bed reactor. The first three types all could be regarded as a “point” operation pattern, the temperature and concentration inside the reactor are in uniform. This property is convenient for FTS kinetic modeling. However, none of them is perfect for the FTS product distribution study. The accumulation of high-carbon-number hydrocarbons in stirred slurry autoclave would seriously disguise the true FTS product selectivity [12,20–22]. The Berty-type recycle reactor is suitable for light hydrocarbon synthesis, but it is hard to be run under real FTS conditions because of the blocking of the agitating shaft by the produced heavy wax. Continuous spinning basket reactor has all the merits of gradientless reactor and has no accumulation effect. However, it is difficult to know the real temperature and the real space velocity of the catalytic bed [23]. The tubular fixed-bed reactor has several distinct advantages in product distribution study, such as easily experimental operating, less product accumulation inside the reactor and shorter time for environment replacement when changing reaction conditions. By suitable catalyst dilution and molten-salt-bath heating, the temperature gradient commonly met in an industrial-scale fixed-bed reactor could be negligible in a laboratory reactor [24].

The flow scheme of the experimental setup used in this study is shown in Fig. 2. It consists of four sections: the feeding, the tubular fixed-bed reactor, the product collection and the product analysis.

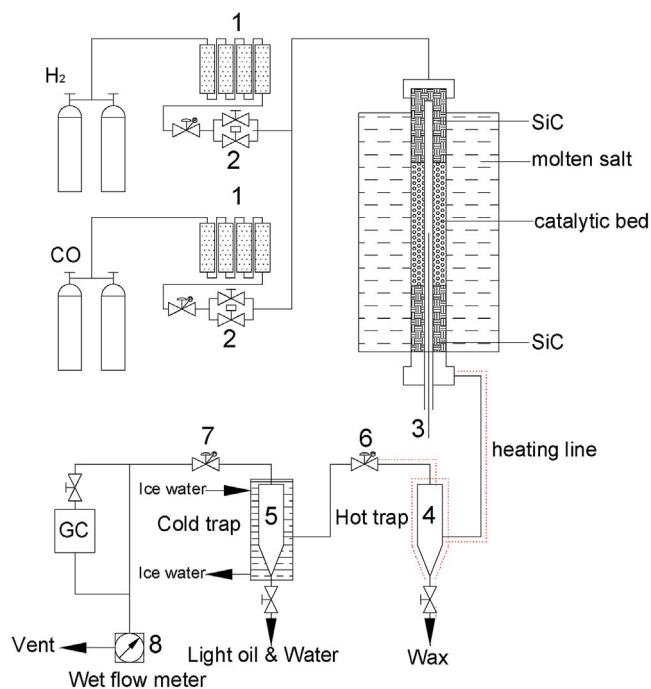


Fig. 2. Flow scheme of the fixed-bed experimental setup. 1. purification unit (de-sulphur, de-oxygen, de-carbonyl, de-water); 2. mass flow controller; 3. thermocouple; 4. hot trap; 5. cold trap; 6 & 7. back pressure regulator; 8. wet flow meter.

In the feeding section, the hydrogen (purity > 99.999%) and the carbon monoxide (purity > 99.999%) passed through a series of purifiers to further remove oxygen, sulfur, carbonyls and water and the flow rates were measured by the thermal mass flow controllers (Brooks 5850E).

The tubular fixed bed reactor is a stainless steel tube (total length 80 cm and internal diameter 1 cm) with a thermal-well (external diameter 0.1 cm) in the center. The reaction heat is removed by a molten salt bath, which is composed of 53% KNO_3 , 40% NaNO_2 and 7% NaNO_3 . The salt bath is stirred strongly by a churning motor to obtain a better heat transfer efficiency and keep acceptable temperature uniformity (see in Fig. 3). Moreover, considering the strongly exothermic property of the FTS reaction, a remarkable dilution of the catalyst bed was performed by inert Silicon Carbide, with the same particle size and mass ratio of 30. The real temperature profile along the catalytic bed is shown in Fig. 3. The hot spot appears in the first 2 cm of the catalytic bed. The maximum temperature gradient is around 1.5°C , which is negligible in the FTS reaction.

The gas-liquid mixture of the reactor effluent enters into a hot trap (typically 170°C), then passes through a back pressure regulator and enters into a cold trap (typically 2°C), as shown in Fig. 2. The non-condensable gases release via a wet flow meter (Ritter TG 1–5). Accordingly, the product collection consists of three parts, the heavy oil (the so-called wax, $\text{C}_6\text{--C}_{70}$ paraffins and olefins) condensed in the hot trap, the light oil ($\text{C}_3\text{--C}_{35}$ paraffins and olefins), the oxygenates (mainly $\text{C}_1\text{--C}_{20}$ alcohols) and the water condensed in the cold trap and the non-condensable gases, based on the boiling range of the reactor effluent, as shown in Fig. 4.

The detailed GC configuration parameters and the flow scheme of the FTS product analysis are shown in Fig. 4. The non-condensable gases include H_2 , CO , CO_2 , $\text{C}_1\text{--C}_{12}$ paraffins and $\text{C}_2\text{--C}_{12}$ olefins. These are analyzed by an online Agilent 7890 B GC equipped with two TCD channels and one FID channel, in which H_2 is detected on TCD1 with a HayeSep Q column ($0.5\text{m} \times 1/8\text{in.}$, mesh size 80/100), CO , CO_2 , CH_4 are detected on TCD2 with a Agilent MolSieve 13X column ($1.83\text{m} \times 1/8\text{in.}$, mesh size 60/80) and the $\text{C}_1\text{--C}_9$ hydrocarbons are detected on FID with a DM-Plot $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ column

Download English Version:

<https://daneshyari.com/en/article/4756765>

Download Persian Version:

<https://daneshyari.com/article/4756765>

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