Hydrocarbon selectivity models for iron-based Fischer–Tropsch catalyst

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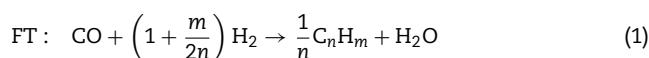
ABSTRACT

Two kinetic models of Fischer–Tropsch product selectivity have been developed based on reaction networks from the literature. The models were fitted to experimental data obtained using commercial iron-based catalyst in a stirred tank slurry reactor and under a wide range of process conditions. Results showed that both of the rival models were able to provide a satisfactory prediction of the experimental product distribution for n-paraffin, 1- and 2-olefin. The simpler of the two models, a reaction network with a single type of active sites and solubility enhanced 1-olefin readsorption term, was chosen as more adequate for practical use.

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1. Introduction

One of the main ways for the production of synthetic hydrocarbon fuels is the Fischer–Tropsch (FT) synthesis process, in which syngas is converted into liquid hydrocarbons over a solid catalyst. Feedstock for the production of syngas can come from several sources, so the FT process is an integral part of the XTL process (XTL = coal-, natural gas-, biomass-to-liquids). Catalysts used in the XTL processes are based on either iron or cobalt. Iron-based catalysts are the catalyst of choice for coal-to-liquids (CTL) process, because of their high activity in water–gas shift reaction (WGS) (Botes et al., 2013).

The two main reactions occurring over iron catalysts can be represented as:

$$FT: \quad CO + \left(1 + \frac{m}{2n}\right) H_2 \rightarrow \frac{1}{n} C_n H_m + H_2O \tag{1}$$

$$WGS: \quad CO + H_2O \leftrightarrow H_2CO_2 \tag{2}$$

A considerable amount of work has been done on modeling of FT and WGS kinetics (van der Laan and Beenackers, 1999a; Zimmerman and Bukur, 1990). The kinetic models of FT synthesis described in the literature may be classified into three categories: (1) models for overall reactant consumption,

(2) models for hydrocarbon product distribution (selectivity models) and (3) comprehensive (or detailed) kinetic models that describe both the overall reactant consumption and hydrocarbon formation rates. The simple reactant consumption models (Zimmerman and Bukur, 1990; Anderson, 1956; Wojciechowski, 1988; Sarup and Wojciechowski, 1989) are useful for initial design and reactor sizing. However, their inability to predict product distribution makes them less useful for more detailed reactor design considerations. This is why simple FT kinetic models are often used in combination with selectivity models in order to get the full set of information about the reactant and product formation rates (Rafiee and Hillestad, 2012).

The first attempt to describe the FT carbon number product distribution utilized the concept of polymerization reaction, which proceeds via addition of a single carbon number monomer. This is the so-called Anderson–Schulz–Flory (ASF) model, where mass balance for adsorbed species from the simplest reaction scheme with n carbon atoms in the molecule leads to the following equation (Anderson et al., 1951):

$$\ln(y_n) = \ln(1 - \alpha) + (n - 1) \cdot \ln(\alpha) \qquad (3)$$

where y_n is the molar fraction of products with n carbon atoms and α is the growth probability factor. The ASF model assumes that α is independent of chain length, meaning that Eq. (3) results in a straight line with slope of $\ln(\alpha)$. It should be noted that the ASF equation does not distinguish between different product types as for instance 1-olefins, 2-olefins, n-paraffins and/or branched hydrocarbons. In addition FT product distribution typically deviates from the ASF prediction in terms of C_1 (higher-than-expected), C_2 (lower-than-expected) and increased growth probability with carbon number (i.e. higher-than-expected amount of heavy hydrocarbons) (van der Laan and Beenackers, 1999a; Claeys and van Steen, 2004; Bartholomew and Farrauto, 2006). These features of the product distribution are most often referred to as the non-ASF behavior.

The first explanations of non-ASF behavior were based on the so-called double-α hypothesis, which assumed that two distinct values of α exist due to availability of two types of active sites (Huff and Satterfield, 1984; Dictor and Bell, 1986; Sarup and Wojciechowski, 1988). The existence of different oxide phases on Fe-based catalysts reinforced this concept (Huff and Satterfield, 1984; Dictor and Bell, 1986). However, observation of non-ASF behavior for Co catalyst, where FT occurs only on Co metallic sites brought this reasoning in question (Botes, 2008). Additional feature of the FT product distribution is that olefin-to-paraffin ratio (OPR) exponentially decreases with carbon number. The double-α models typically do not differentiate between paraffin and olefin products, i.e. they only consider total hydrocarbons. A concept that offered explanation for both OPR and non-ASF features was olefin readsorption (Herington, 1946; Novak et al., 1982; Iglesia et al., 1991). The initially formed 1-olefin molecules are known to participate in secondary reactions, one of which is readsorption followed by continued chain growth. If 1-olefin readsortion is set to be dependent of chain length, due to increase in concentration of 1-olefins with increase in molecular weight, both non-ASF and OPR can be predicted. This is related to increased residence time of larger molecules, which in turn is caused by their lower diffusivity, increased

physisorption strength and increased solubility. Most of the selectivity models in the literature have used this concept and it provides a good prediction of experimental results (Iglesia et al., 1991; Schulz and Claeys, 1999; Kuipers et al., 1996; Zimmerman et al., 1992).

More recently, the comprehensive kinetic models of FT based on Langmuir–Hinshelwood–Hougen–Watson (LHHW) approach, as well as models based on single-event methodology, have been examined in the literature (Lox and Froment, 1993; Wang et al., 2003; Yang et al., 2003; Teng et al., 2006; Todic et al., 2013a,b, 2014; Lozano-Blanco et al., 2008, 2011). However, hydrocarbon selectivity models have significantly higher precision in predicting product distribution for a given set of conditions and they have a smaller number of adjustable parameters than the comprehensive kinetic models.

The focus of the present study is on development of selectivity models for the prediction of FT product distribution, including n-paraffins and 1- and 2-olefins. Two models were derived using reaction networks of different complexity and including 1-olefin readsorption approach. The first model is based on the one-site van der Laan and Beenakers' model (van der Laan and Beenackers, 1999b) with the extension to 2-olefin formation, and the second model is a two-site model of Nowicki et al. (2011). Model derivation included a novel approach, i.e. reparameterization, which reduced the number of adjustable parameters of both models. In addition, the VLE calculation was conducted independently in order to determine the 1-olefin solubility parameter c, thereby removing the need for estimation of this parameter from the rates data.

2. Experimental procedures and results

Commercial precipitated iron FTS catalyst obtained from Ruhrchemie AG (Oberhausen-Holten, 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. (1977). It has been tested extensively in our Laboratory (Zimmerman and Bukur, 1990; Zimmerman et al., 1992; Bukur et al., 1990, 1995; Ma et al., 2004), and was also used in previous studies of the kinetics of FTS by Lox and Froment (1993) and van der Laan and Beenackers (1998, 1999b). Nominal composition of the catalyst is 100 Fe/5 Cu/4.2 K/25 SiO$_2$ (in parts per weight), whereas, its composition by atomic absorption spectrometry (AAS) was found to be 100 Fe/5 Cu/4 K/27 SiO$_2$ (Bukur et al., 1995). Surface area and pore volume of calcined Ruhrchemie catalyst were 290 m^2/g and 0.62 cm^3/g, respectively (Bukur et al., 1995, 1996).

Three tests (runs) were conducted in a 1 dm^3 stirred-tank slurry reactor (Autoclave Engineers). Details on the experimental set up, operating procedures, and product quantification can be found elsewhere (Zimmerman and Bukur, 1990; Bukur et al., 1990, 1996; Olewski, 2008). Briefly, 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. After leaving the reactor, the exit gas passed through a series of high and low (ambient) pressure traps to condense the 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