Fischer-Tropsch Synthesis Product Selectivity over an Industrial Iron-based Catalyst: Effect of Process Conditions

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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 towards 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.

Keywords: Fischer-Tropsch synthesis; slurry reactor; product selectivity; iron-catalyst; coal-to-liquid.

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 H_2/CO ratio below 2, the latter being an approximate stoichiometric H_2/CO ratio needed to produce hydrocarbons according to equations (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 C_{10}), 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 C_3 before reaching an asymptotic value at higher carbon number range (typically above C_{15}) [7]. Typical deviations from the ASF distribution include higher methane and lower C_2 [8, 9]. Another important feature of FTS products is the ratio between various main products (n-paraffin/1-olefin and 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-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. [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 hours.

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 Figure 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 noncondensable 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 ($H_2/CO = 0.67$ representative of coal derived synthesis gas and $H_2/CO = 2$ representative of syngas 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 ($X_{CO} = 9$ to 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).

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

where $n = 1 - 4$. The selectivity to C_{5+} is then expressed as:

$$S_{C_{5+}} = 100\% - \sum_{n=1}^4 S_{C_n} \quad (9)$$

The above formulas assume that there is no carbon dioxide in the feed.

- Mole fractions of hydrocarbons (product distribution) with n carbon atoms

$$y_n = \frac{F_n}{F_{HC,tot}} \quad (10)$$

where F_n is the molar flowrate of hydrocarbons with n carbon number and $F_{HC,tot}$ is the flowrate of all hydrocarbons.

The chain growth probabilities for hydrocarbons having n carbon atoms (α_n) were calculated as:

$$\alpha_n = \frac{\sum_{i=n+1}^{\infty} F_i}{\sum_{i=n}^{\infty} F_i} \quad (11)$$

1-olefin to n -paraffin and 2-olefin to total olefin ratios for different chain lengths were calculated as follows:

$$1-olefin / n-paraffin = \frac{F_n^{1-olefin}}{F_n^{n-paraffin}} \quad (12)$$

$$2-olefin/total\ olefin = \frac{F_n^{2-olefin}}{F_n^{olefin}} \quad (13)$$

3. Results and discussion

Analyzing the effect of process conditions (temperature, pressure, reactant feed ratio and conversion level) on FTS product formation selectivity over Fe-based catalyst is complex because of the competing effects of several parallel reactions, including primary FTS reaction, secondary 1-olefin reactions and WGS. Apparent product distribution features, such as growth probabilities, 1-olefin-to-n-paraffin ratios and selectivities with carbon number, are dependent on the mutual interplay of the kinetics of these reactions. With Fe-based catalysts the effect of WGS is very significant. This reaction affects concentrations (partial pressures) of CO, H₂, CO₂ and H₂O in the system, which in turn has an impact on kinetics of both primary FTS and 1-olefin secondary reactions.

Because of this complexity and unknown nature of kinetics over Fe-based catalysts, it is impossible to design an experiment in which only one process parameter affecting kinetics is varied, while all others are kept constant. The observed FTS behavior will therefore reflect a lumped effect of several process parameters (e.g. increasing T and changing partial pressures of reactants). Dry [13, 29] has shown that FTS selectivity correlates well with H₂/CO ratio in the reactor for low temperature FTS (LTFT) at Sasol. Therefore, when assessing the effect of process conditions on selectivities it is important to make comparisons at nearly constant values of this ratio in the reactor.

3.1 Effect of time on stream on catalyst activity and selectivity

The catalyst was tested initially at baseline conditions (533 K, 1.5 MPa, 4 NL/g-Fe/h, $H_2/CO = 0.67$) in order to check reproducibility of data collected in three different runs. The catalyst in Runs 1 and 2 was tested at baseline conditions up to 80 h on stream, whereas in Run 3 from 50 to 73 h on stream. Results from all three tests at the baseline conditions and during the initial period are shown in Figure 2. CO conversion (Figure 2a), methane and C_{5+} hydrocarbon selectivities (Figure 2b) during the first 80 h of testing were very similar in all three tests. It was observed that conversion and selectivity approach stationary values after about 50-60 h on stream. Ruhrchemie catalyst was studied extensively in our laboratory [14, 28, 30-32], and it was found that selectivity does not change much after 50-60 h on stream, even though conversion may increase or decrease slightly with time (up to 100 h on stream) while maintaining constant process conditions. Small changes in conversion do not have significant effect on selectivity.

Baseline conditions were periodically repeated in all three runs in order to assess the extent of catalyst deactivation. CO conversion and selectivities at the baseline process conditions and different times on stream are shown in Figure 3. Catalyst activity (CO conversion) decreased with time in all three tests (Figure 3a). Methane and C_5^+ selectivities were relatively constant with time (Figure 3b). In previous studies [14, 15, 33] it was found that methane and C_{5+} selectivity slowly increased and decreased, respectively, with time on stream (TOS). Also variation of product distribution as a function of carbon number with time was examined in Run 1 (mass balances 1, 7 and 10 in Table 1). Total hydrocarbon and 1-olefin/n-paraffin ratio for these conditions are shown in Figures 4a and 4b, respectfully. It can be seen that the product distribution did not change significantly with time. From this we conclude that data at other process conditions were not significantly affected by catalyst deactivation.

3.2 Water-gas-shift reaction

A measure of WGS activity is the amount of CO₂ formed in the reactor. In order to be able to understand and at least partially eliminate the effect of WGS reaction on FTS product distribution we will first analyze how WGS activity varies with process conditions.

A useful property to look at when studying WGS is the usage ratio (UR):

$$UR = (\text{Moles of H}_2 \text{ consumed}) / (\text{Moles of CO consumed}) \quad (14)$$

In the absence of the WGS reaction, the usage ratio is approximately 2 (Eqs. 1 and 2). In the case of high WGS activity, where all water produced by FTS is consumed by the WGS reaction, the usage ratio is 0.5 and the CO₂ selectivity is 50% (assuming that CO is not consumed in any other reactions except hydrocarbon formation and WGS).

The effect of temperature and conversion of the limiting reactant (H₂ for H₂/CO = 0.67 feed gas, CO for H₂/CO = 2 feed gas) on the extent of WGS reaction is shown in Figures 5a and 5b. The usage ratio decreases whereas the CO₂ selectivity increases with an increase in conversion (at constant temperature) or with an increase in temperature (at constant conversion of the limiting reactant). This trend is the same regardless of feed composition (H₂/CO = 0.67 in Fig. 5a, or H₂/CO = 2 in Fig. 5b). From the stoichiometry it is expected that the extent of WGS reaction (secondary or consecutive reaction) will increase with increase in conversion, which is manifested in a decrease of the usage ratio and increase in CO₂ selectivity. The increase in WGS activity (higher CO₂ selectivity and lower UR) with increase in temperature (at constant conversion) is a kinetic effect. Reaction pressure has the opposite effect, i.e. the extent of the WGS reaction increases (lower UR and higher CO₂ selectivity) with decrease in total pressure (data not shown).

Changes in the usage ratio result in changes in the exit (i.e. reactor) H₂/CO ratio as shown in Figure 6. These data were obtained under different process conditions (T, P and space

velocity) but all data are well represented by the two curves, one for each of the two H_2/CO feed ratios. As the extent of WGS reaction increases (i.e. UR decreases) the reactor H_2/CO ratio increases dramatically for $H_2/CO = 2$ feed gas, and only slightly for $H_2/CO = 0.67$ feed gas. This in turn has a significant effect on FTS selectivity as shown in the next section.

3.3 Effect of H_2/CO ratio on FTS selectivity

For the inlet H_2/CO ratio of 0.67, the limiting reactant is hydrogen, while in the case of $H_2/CO = 2$ the limiting reactant is carbon monoxide. The H_2/CO ratio inside the reactor corresponds to the ratio at the outlet. In this part we will only compare the effect on selectivity of low vs. high H_2/CO ratio, which remain far enough apart regardless whether we are looking at inlet or outlet reactant ratios.

Our data shows that the increase in H_2/CO feed ratio results in higher selectivity of light products (CH_4 and C_2-C_4) whereas C_{5+} selectivity decreases (Figure 7a). These trends are typically observed with all FTS catalysts [8, 13,14-16, 34]. This is related to the decrease of chain growth probability with increasing H_2/CO ratio both at the inlet and inside the reactor (Figure 7b). Donnelly and Satterfield [15] conducted studies with unpromoted Fe and Ruhrchemie catalysts in a slurry reactor and reported that chain growth probabilities α_1 and α_2 (based on so called double alpha model [54]) depend very little on H_2/CO ratio in the reactor (range of 0.3-3). However, the data shown for unpromoted Fe have a great deal of variation for a given value of H_2/CO ratio, whereas no data have been presented for the Ruhrchemie catalyst. Dictor and Bell [16] conducted studies with unpromoted and potassium promoted Fe catalysts in a slurry reactor under differential conditions (CO conversion less than 5%). They found that α (for C_1-C_7 hydrocarbons) decreases with increasing H_2/CO ratio on both catalysts (the magnitude of change being smaller for K promoted catalyst). Liu et al. [17] conducted studies with

potassium promoted Fe/Mn catalyst in a spinning basket reactor, and their results show that increase in H_2/CO ratio leads to preferential chain termination manifested in increase of CH_4 and light hydrocarbons, and lower content of high molecular weight products (ASF plots). A logical interpretation for these observations is that the increase in H_2/CO causes an increase in H surface coverage in relation to monomer coverage resulting in an increased rate of chain termination.

Our results show that OPR decreases significantly and selectivity towards 2-olefins increases with increasing H_2/CO ratio (Figure 7c) which is in agreement with previous results obtained in our laboratory with the same catalyst [14, 35]. Donnelly and Satterfield [14] reported decrease in OPR, and increase in 2-olefin content for C_4 hydrocarbons only, with increase in the reactor H_2/CO ratio. Dictor and Bell [16] reported that the percentage of olefins decreases with an increase in partial pressure of H_2 (at constant partial pressure of CO) for K promoted Fe catalyst, but did not present any data for 2-olefin selectivity due to the small amounts of products produced under differential conditions. Liu et al. [17] reported increase in hydrogenation (less olefins in C_2 - C_4 carbon number range) with increase in H_2/CO feed ratio. The decrease in 1-olefins is caused by increases in both primary and secondary hydrogenation reactivity. An effect that could have influence on the decrease of OPR with increasing H_2/CO is the reduction in CO partial pressure, due to inhibiting properties of CO to secondary hydrogenation. For the conditions shown in Figure 7 the CO conversion was kept constant with increasing H_2/CO , which meant SV was increased simultaneously. Lower residence time at high H_2/CO condition would have decreased the secondary reactivity of 1-olefins, i.e. increased OPR. However since OPR decreased it is evident that increasing H_2/CO had a more significant effect compared to the residence time.

3.4 Effect of temperature on FTS selectivity

The effect of temperature for Fe catalyzed FTS reaction has been reported many times in the literature. The consensus is that with increasing temperature the amount of light products increases while that of heavy products decreases [13-15,19, 35, 36], which is linked to decrease in chain growth probability. However, this effect is much more pronounced with cobalt and ruthenium than with iron FTS catalysts [2, 37]. On the other hand, the increase of T is sometimes reported to increase olefin content [15, 16, 38], however the opposite trend was observed as well [15, 39, 40]. Our data show that α_n typically slowly decreased with increase in T (Figure 8b), for a given pressure and reactant feed ratio (noting that the reactant ratio inside the reactor is relatively constant). This explains trends shown in Figure 8a, where methane and C₂-C₄ selectivities increase, whereas C₅₊ selectivity decreases with increasing T.

The growth probability is kinetically determined by the ratio between rates of chain propagation ($R_{p,n}$) and termination reactions ($R_{t,n}$):

$$\alpha_n = \frac{R_{p,n}}{R_{p,n} + R_{t,n}} \quad (15)$$

The rates of these surface reactions are determined by corresponding rate constants and surface coverages of monomeric species and atomic hydrogen, which all vary with changing temperature. The main effect of temperature would be to change rate constants of FTS chain propagation and termination that determine α_n (Eq. 15). The reaction with higher activation energy will respond faster to changes in T. The implication of decreasing α_n with T is that the chain termination has a higher activation energy than the chain propagation. However, relatively slow decrease of α_n with temperature (within the tested range 493-533 K) suggests that the difference between the two activation energies is relatively small.

Our data showed mixed results for OPR variation with changing T, which is consistent with literature studies [15, 16, 38, 39]. The analysis of T effect on OPR is difficult because of a number of temperature related processes that would affect OPR. The effects that could, along with others, cause a change of OPR with increasing T are:

- 1) Higher activation energy of chain hydrogenation (n-paraffin formation) compared to desorption (1-olefin formation) [41-43] would cause a decrease of OPR with increased T.
- 2) Increased FTS reaction rate with T causes increase in partial pressure of water, which inhibits secondary olefin reactions, leading to higher OPR [44, 45].

It should also be pointed out that residence time in our study decreased with increasing T, which would favor the increase of OPR due to lower extent of secondary olefin reactions. Also interesting is that even though the OPR remained relatively constant with temperature, the amount of 2-olefins increased (Figure 8c). The same qualitative trend with respect to 2-olefin selectivity was reported in other studies with Ruhrchemie catalyst [14, 15]. This could mean that the activation energy for 2-olefin formation is higher compared to those for 1-olefin and n-paraffin formation.

3.5 Effect of pressure on FTS selectivity

It is well known that total pressure has a positive effect on FTS reaction rate [13, 17, 39, 46]. A positive effect has also been reported on FTS product selectivity, decreasing methane and increasing C₅₊, for cobalt-based catalysts [33, 46]. For iron catalysts the same effect has been reported [47], but the influence of total pressure on selectivity for this catalyst is much smaller than for cobalt [48]. Botes et al. [2] studied the effect of syngas pressure on methane selectivity at constant outlet H₂/CO of 2 showing no variations of methane selectivity between 4 and 25 bar.

Similar trend, negligible effect of pressure on FTS selectivity over Fe catalysts, was reported by Dry [13].

Figure 9 shows the detailed product distribution features as a function of total pressure at 1.5 and 2.5 MPa (temperature and inlet feed ratio are kept constant and conversion values are similar). Selectivity towards light products (methane and C₂-C₄) decreased and C₅₊ selectivity increased with total pressure (Figure 9a). These changes can be related to variations in α_n (Figure 9b), which shows slight increase with increasing total pressure. The reason for this behavior can be explained in terms of kinetics as a decrease of hydrogen to carbon monoxide coverage ratio. Dinse et al. [46] showed that the decrease of hydrogen to carbon monoxide coverage ratio favors propagation over chain termination via hydrogenation, therefore causing increase in α_n .

We would like to point out that for conditions in our experiments the outlet H₂/CO ratio was not constant at different total pressure; it decreased with increasing P. This would also cause a decrease of H/CO surface coverage ratio and the observed product selectivity variations. Therefore, it can be expected that at a constant outlet H₂/CO ratio the effect of changing P on selectivity would have been much lower, as reported by Botes [2].

OPR increases with increasing P (Figure 9c), which can be caused by several processes:

- 1) Decrease in primary n-paraffin formation by chain hydrogenation due lower outlet H₂/CO ratio.
- 2) Decrease in secondary 1-olefin reactions due to lower outlet (and surface) H₂/CO ratio, because H₂ promotes secondary hydrogenation and CO suppresses secondary reactions altogether [49].
- 3) Higher water partial pressure due to higher total pressure suppresses secondary reactions of 1-olefins [45].

Increased partial pressure of in-situ formed 1-olefins would have increased rate of their secondary reactions, however this effect seems to be minor in comparison to factors that suppress secondary reactions and increase OPR. The 2-olefin content, i.e. 2-olefin/total olefin ratio, decreased with increasing total pressure (see Figure 9c). Dictor and Bell [16] and Egiebor et al. [50, 51] reported that internal olefins are formed through secondary reactions of 1-olefins over iron-based catalysts. This explanation would be consistent with our results, since 2-olefins content is decreasing, while OPR is increasing, with increasing pressure.

3.6 Effect of conversion level on FTS selectivity

Conversion level at fixed values of temperature, pressure and feed ratio was controlled by varying the space velocity (SV) in 0.5 to 23.5 NL/(g_{cat}*h) range. CO conversions from 9 to 84% were achieved. For the majority of data varying space velocity did not have a significant effect on hydrocarbon product selectivity (Figures 10a and 10b), i.e. typically CH₄ and C₅₊ selectivity remains relatively constant at different conversions (i.e. residence time). Bukur et al. [14] reported the same result. This is consistent with relatively constant values of chain growth probabilities at different conversions (Figure 11a), which was also found in other studies with potassium promoted Fe catalysts [15, 16]. OPR decreases with increase in residence time (Figure 11b) due to 1-olefin secondary reactions (hydrogenation, isomerization and readsorption). Very small changes in OPR with increase in SV were reported by Donnelly and Satterfield [15] and Dictor and Bell [16]. From Figure 11b we see that the amount of 2-olefins in the products increases with increased residence time, which would be expected if 2-olefins are formed by isomerization of 1-olefins.

3.7 Oxygenate formation

In addition to hydrocarbons, products containing oxygen atoms (mainly alcohols) are formed as well. Oxygenates are a minor product of FTS and their content can vary depending on the process conditions [8, 13].

Figure 12a shows the molar flowrates of different chain length oxygenates together with flowrates of hydrocarbon products. It is clear that oxygenates are minor products compared to n-paraffin and 1-olefin. However, some studies suggest that oxygenates cannot be neglected when analyzing the product distribution of low weight molecules, mainly C_1 and C_2 , since neglecting them could lead to more significant deviations from ASF [52]. This can be seen, to some extent, in our results as well (Figure 12b), where inclusion of oxygenates leads to smaller deviations from ASF distribution (notably C_1 and C_2 products) compared to hydrocarbons only. However, overall non-ASF behavior (different slope for C_{10+} products) is unaffected by the inclusion of oxygenate products into the product distribution plot. It is also interesting to note that oxygenates and olefins have a different slope compared to n-paraffin in the range above C_9 (Figure 12a). This refers to the so-called “break in the ASF” or non-ASF behavior. Wojciechowski [53] interpreted this as proof that n-paraffins have two different termination steps, one with addition of hydrogen atoms and one with the addition of methyl group to the growing chain, while olefin and oxygenates only have one. Huff and Saterfield [54] hypothesized that some molecules (including oxygenates, olefins and lighter paraffins) are created on a separate type of active sites, compared to the heavier paraffins. Additional explanations for these differences in slopes with carbon number are the existence of secondary reactions of 1-olefin and oxygenates [10, 55], as well as the dependence of 1-olefin desorption rates on chain length [56-58]. It should be noted, though, that the latter theory was only applied to 1-olefins and not to oxygenates.

The oxygenate products formed in FTS are mainly low molecular weight oxygenates and the amount of formed oxygenates quickly declines with carbon number. The oxygenate slope in the ASF plot is steeper compared to n-paraffin and 2-olefin, and is similar to that of 1-olefins (see Figure 12a). This could suggest some similarities in the formation of oxygenates and 1-olefins in FTS [59]. Both species are well-known to participate in secondary reactions. Tau et al. cofeeding study [55], as well as other studies (see Ref. [60] and therein), showed that externally added n-alcohols undergo hydrogenolysis to corresponding n-paraffin, dehydrogenation to aldehyde or ketone, as well as reincorporation and continued chain growth to hydrocarbons. The chain-length dependency of n-alcohol secondary reactions is likely the reason for the lack of higher molecular weight oxygenate products. Our results show that oxygenate flowrates decrease with increasing residence time (Figure 13), which is an indirect proof of oxygenate secondary reactivity. This is consistent with results obtained at Sasol with Fe catalysts [13].

The oxygenate content can be calculated in relation to hydrocarbons as:

$$Oxygenates(wt.%) = 100\% \times \frac{\dot{m}_{Oxygenates}}{\dot{m}_{Oxygenates} + \dot{m}_{HC,total}} \quad (16)$$

where $\dot{m}_{Oxygenates}$ and $\dot{m}_{HC,total}$ are mass flowrates of oxygenates and hydrocarbons, respectively.

The effect of process conditions on oxygenate formation is rarely reported in the literature due to the difficulty to analyze relatively low amounts of these products. Our results show decrease in oxygenate content with increasing temperature and an increase with increasing reactant feed ratio (Figure 14) which is consistent with [13]. An increase in oxygenates content was reported for higher pressures [8, 13], however our results showed complex behavior for pressure variations. This could be related to variations of partial pressures with the changing extent of WGS.

4. Conclusions

Variations in FTS hydrocarbon selectivity, as a result of changes in process conditions, are related to changes in chain growth probabilities. Studying these probabilities can lead to better understanding of intrinsic kinetics of FTS surface reactions. In this study we showed that increasing temperature and H_2/CO feed ratio decreases the growth probabilities, leading to increased methane and lower C_{5+} selectivity. Pressure increase was shown to have a positive, albeit slight, effect on selectivity. The conversion effect on selectivity is complex and selectivity towards methane and C_{5+} does not seem to be significantly affected by variations in residence time. Considering all of the conditions tested we can conclude that values of C_1 and C_2 growth probabilities are close to those of C_{3+} species and do not exhibit significantly different behavior at different process conditions. Unlike for cobalt-based FTS catalysts where C_1 is the dominant cause for selectivity changes [34], with iron catalyst all of the growth probabilities seem to change in parallel and contribute to selectivity shifts.

Process conditions determine the content of different hydrocarbon species, primarily n-paraffin, 1- and 2-olefin, as well as oxygenate formation. As seen from variations of 1-olefin/n-paraffin ratio, increasing residence time and H_2/CO ratio favored secondary 1-olefin reactivity and resulted in a lower OPR. The effect of pressure and temperature on 1-olefin content was shown to be smaller and more complex. 2-olefin content in olefins increases with increasing residence time, temperature and H_2/CO ratio, while pressure increase has the opposite effect. Oxygenate formation was most affected by temperature and H_2/CO ratio variations. Decrease of oxygenate content at higher residence time is related to their participation in secondary reactions.

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Figure 14 – Effect of process conditions on the oxygenate selectivity: a) Effect of temperature; b) Effect of inlet H₂/CO ratio.

Table 1

Run	No.	TOS	T	P	Inlet H ₂ /CO	Outlet H ₂ /CO	SV	X _{CO}	X _{H2}	X _{CO+H2}	UR	P _{CO}	P _{H2}	P _{H2O}	P _{CO2}	Selectivity			
		h	K	MPa			NL/g- Fe/h	%	%	%	-	MPa	MPa	MPa	MPa	CH ₄	C ₂ -C ₄	C ₅₊	CO ₂
																C-atom %			mol. %
1	1 ^b	78	533	1.50	0.67	0.58	4.0	54	60	57	0.74	0.63	0.37	0.08	0.33	4.0	19.4	76.6	43.2
	2	101	533	1.50	0.67	0.84	1.7	84	80	82	0.64	0.31	0.26	0.06	0.71	3.0	12.4	51.3	29.8
	3	126	533	1.50	0.67	0.56	9.2	27	39	31	0.98	0.82	0.46	0.06	0.11	3.8	19.4	76.8	32.8
	4	164	513	1.50	0.67	0.54	2.0	39	51	45	0.88	0.76	0.41	0.09	0.18	2.7	13.5	83.8	32.1
	5	215	513	1.50	0.67	0.58	1.0	56	62	59	0.74	0.62	0.36	0.07	0.36	3.3	18.7	77.9	40.0
	6	238	513	1.50	0.67	0.58	5.5	14	25	18	1.22	0.87	0.50	0.05	0.04	3.0	15.5	81.5	20.2
	7 ^b	270	533	1.50	0.67	0.56	4.0	46	54	50	0.79	0.69	0.39	0.08	0.26	4.3	20.7	75.0	41.3
	8	310	513	1.50	2.00	2.63	4.2	46	29	36	1.26	0.34	0.89	0.11	0.08	7.2	23.6	69.2	24.9
	9	338	513	1.50	2.00	2.18	10.8	22	15	18	1.35	0.43	0.93	0.06	0.02	2.9	16.0	81.0	19.9
	10 ^b	505	533	1.50	0.67	0.56	4.0	46	55	50	0.80	0.69	0.39	0.08	0.25	4.2	20.0	75.8	41.3
	11	606	533	2.25	0.67	0.50	6.1	36	52	43	0.96	1.13	0.57	0.14	0.25	4.1	21.1	74.8	38.0
	12	654	533	2.25	0.67	0.79	1.0	84	81	83	0.65	0.43	0.34	0.17	1.01	4.5	19.9	75.6	45.3
2	13	92	533	1.50	2.00	5.27	7.1	77	39	52	1.02	0.17	0.89	0.14	0.19	9.2	24.5	66.3	35.9
	14	122	533	1.50	2.00	3.91	10.1	66	34	46	1.02	0.23	0.89	0.14	0.15	8.4	24.8	66.8	34.1
	15	146	533	1.50	2.00	2.54	23.5	41	25	32	1.22	0.36	0.90	0.11	0.07	7.8	28.2	64.0	29.4
	16	191	513	1.50	2.00	2.92	5.8	55	34	42	1.25	0.30	0.87	0.15	0.10	6.3	23.8	69.9	27.9
	17	240	533	2.50	0.67	0.48	6.7	43	60	50	0.93	1.32	0.63	0.21	0.36	2.8	17.4	79.8	35.0
	18	268	533	2.50	0.67	0.53	17.1	20	37	27	1.24	1.51	0.80	0.15	0.10	3.6	20.4	76.0	26.7
	19	313	533	2.50	0.67	0.54	2.0	70	76	72	0.73	0.88	0.47	0.23	0.83	3.4	19.7	76.9	41.7
3	20	101	493	1.50	0.67	0.56	4.1	11	25	16	1.55	0.89	0.50	0.05	0.02	3.0	16.2	80.8	18.8
	21	143	493	1.50	0.67	0.50	0.5	34	51	41	1.00	0.79	0.39	0.11	0.14	3.2	21.5	75.3	35.1
	22	170	493	1.50	2.00	2.03	9.5	13	12	13	1.78	0.47	0.95	0.04	0.01	5.2	22.1	72.6	11.6
	23	198	493	1.50	2.00	4.17	0.6	72	42	54	1.16	0.18	0.77	0.29	0.14	5.4	22.2	72.4	27.6
	24	238	533	0.80	2.00	8.52	1.5	84	32	54	0.76	0.06	0.49	0.05	0.13	11.0	24.9	64.1	39.5
	25	268	533	0.80	2.00	2.42	9.0	35	21	25	1.22	0.21	0.50	0.03	0.03	7.1	23.4	69.6	31.0
	26	292	513	0.80	0.67	0.61	5.5	9	17	13	1.25	0.47	0.29	0.02	0.01	3.1	16.1	80.7	27.9
	27	318	513	0.80	0.67	0.61	0.7	50	54	54	0.73	0.34	0.21	0.04	0.17	2.9	15.5	81.6	45.8

Note: b – baseline condition.

Figure 1

Figure 2a

Figure 2b

Figure 3a

Figure 3b

Figure 4a

Figure 4b

Figure 5a

Figure 5b

Figure 6

Figure 7a

Figure 7b

Figure 7c

Figure 8a

Figure 8b

Figure 8c

Figure 9a

Figure 9b

Figure 9c

Figure 10a

Figure 10b

Figure 11a

Figure 11b

Figure 12a

Figure 12b

Figure 13

Figure 14a

Figure 14b

Component carbon number distribution