



# Effect of process conditions on the product distribution of Fischer–Tropsch synthesis over a Re-promoted cobalt–alumina catalyst using a stirred tank slurry reactor



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## ABSTRACT

The effects of process conditions on Fischer–Tropsch synthesis (FTS) product distribution were studied using a 1-L stirred tank slurry reactor and a 0.48%Re–25%Co/Al<sub>2</sub>O<sub>3</sub> catalyst. It was found that the chain growth probability of C<sub>1</sub> intermediate ( $\alpha_1$ ) has the most dominant effect on CH<sub>4</sub> and C<sub>5+</sub> selectivity.  $\alpha_1$  was found to be highly dependent on process conditions. Relatively constant values of C<sub>2+</sub> growth probabilities with reactor residence time, as well as other process variables, suggest that 1-olefin readsorption has a minor effect on product selectivities. A low value of  $\alpha_1$  and its different response to variations in process conditions, compared to higher chain growth probabilities, seems to support a hypothesis that a higher-than-expected yield of methane is caused by at least two separate methane formation pathways. Understanding these pathways and ways to suppress excess methane formation is a key factor in obtaining higher C<sub>5+</sub> selectivity.

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## 1. Introduction

Fischer–Tropsch synthesis (FTS) is a heterogeneous catalytic reaction used for the production of a distribution of hydrocarbons from a mixture of carbon-monoxide and hydrogen (i.e., syngas); these hydrocarbons can be upgraded to produce high quality diesel, jet fuels, lubricants, and waxes, among other products. The main products of the reaction are n-paraffins and 1-olefins, but other species, such as branched isomers, internal olefins and various oxygenates are present in minor amounts as well. Cobalt-based catalysts are used in commercial FTS reactors for gas-to-liquids (GTL) processes, because they exhibit high activity and good selectivity toward the desired C<sub>5+</sub> products, and have low intrinsic activity for the water–gas-shift reaction.

FTS is a polymerization type reaction and is characterized by a chain growth mechanism in which a C<sub>1</sub> surface species (a monomer) is inserted into the growing C<sub>n</sub> chain, where *n* is the number of carbon atoms in a molecule. This feature of FTS has been used in the past to define the product distribution and predict the selectivity trends of hydrocarbons as a function of the number of carbon

atoms in the molecule. Molar fractions of hydrocarbons can be calculated using the Anderson–Schulz–Flory (ASF) model [1]:

$$y_n = (1 - \alpha) \cdot \alpha^{n-1} \quad (1)$$

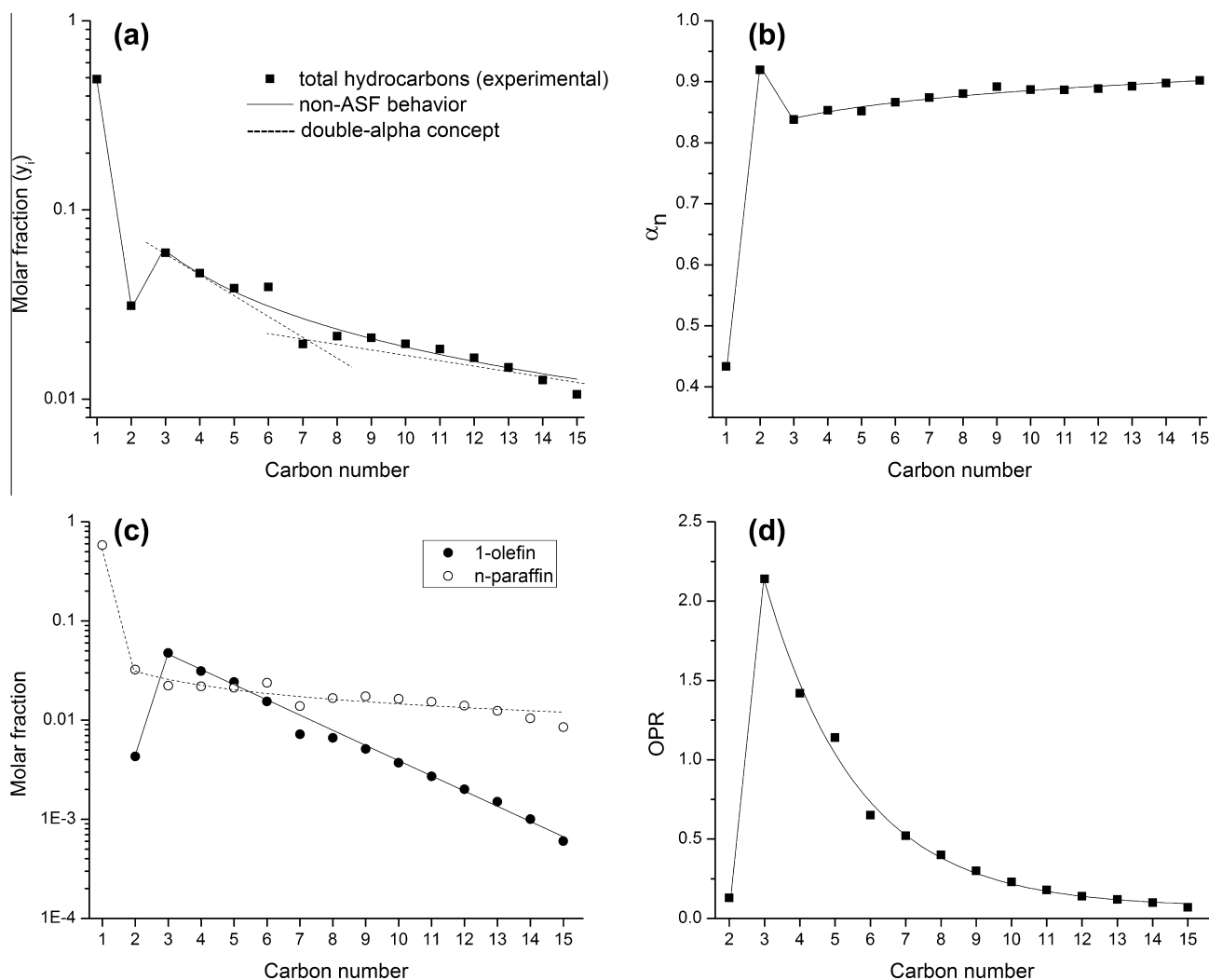
where molar fraction of hydrocarbons with *n* carbon atoms *y<sub>n</sub>* is defined by its length (*n*) and chain growth probability  $\alpha$ , which is independent of chain length. This model is most often presented in its logarithmic form:

$$\log(y_n) = \log\left(\frac{1 - \alpha}{\alpha}\right) + \log(\alpha) \cdot n \quad (2)$$

Eq. (2) shows that the slope in a  $\log(y_n)$  vs. *n* plot will be equal to  $\log(\alpha)$ , i.e., a constant slope for the entire distribution. However, the FTS product distribution very seldom follows the classical ASF distribution and regularly reported deviations from this model are (Fig. 1a): a higher-than-expected fraction of methane, a lower-than-anticipated yield of C<sub>2</sub> (caused by the low fraction of ethene), and a positive bend in the ASF plot (i.e., greater-than-expected yield of higher hydrocarbons due to an increase in chain growth probability with carbon number). These features are known as non-ASF behavior and the underlying causes have been the topic of debate for several decades now. One of the initial explanations was that the non-ASF behavior is caused by the superposition of two distinct growth probabilities [2,3], where one governs the product distribution in the low, and the other one in the high, carbon number range,

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**Fig. 1.** FTS product distribution over 0.48%Re–25%Co/Al<sub>2</sub>O<sub>3</sub> (at 493 K, 1.5 MPa, H<sub>2</sub>/CO = 2.1, 8 NL/g<sub>cat</sub>/h): (a) log-scale molar fractions ( $y_i$ ) vs. carbon number; (b) chain growth probabilities with carbon number ( $\alpha_n$ ); (c) log-scale molar fractions of 1-olefin and n-paraffin vs. carbon number; and (d) 1-olefin-to-n-paraffin ratio (OPR) with carbon number.

with overlap in the C<sub>5</sub>–C<sub>10</sub> range (Fig. 1a). Potential reasons for double- $\alpha$  behavior were thought to be the existence of two types of active FTS sites and/or two separate reaction pathways [4,5]. It should be noted that research initially focused on Fe-based catalysts, which exhibit a very clear bend in the product distribution. Due to a relatively smaller bend in the product distribution of Co-based catalysts as compared to Fe, and a general lack of interest in these catalysts at the time, deviations from the ASF distribution for this catalyst were reported later [6]. Secondary reactions of initially formed olefins (hydrogenation, isomerization and readsorption), an interesting general feature reported over all FTS catalysts, were also proposed as a potential explanation of the non-ASF behavior [7]. The concept was that the secondary readsorption of olefins, followed with continued chain growth, causes the shift toward heavier products. A mathematical model based on this theory, proposed by Novak et al. [8], showed that if the majority of olefins readsorbed and did not hydrogenate or isomerize, the result would be a non-ASF distribution. Additional refinements of this theory were made upon introducing the assumption that secondary reactions of olefins are dependent on chain length, i.e., that they are enhanced by longer reactor residence times of high molecular weight 1-olefins due to their lower diffusivities, higher solubilities in FTS wax, and/or stronger physisorption characteristics [9–14]. This meant that the growth probability increasing with carbon number (Fig. 1b) could

be explained by enhanced 1-olefin readsorption. The experimental product distribution typically shows that 1-olefin formation has a much steeper slope with carbon number than n-paraffin fractions (Fig. 1c), which when summed up causes the total hydrocarbon distribution to exhibit non-ASF features (Fig. 1a). In addition, the finding that the ratio of 1-olefins to n-paraffins exponentially decreases with carbon number (Fig. 1d) reinforced the utility of the olefin readsorption concept.

With the exception of the non-ASF behavior of methane, most of the typical changes in the FTS product distribution with process conditions (e.g., increase in C<sub>5+</sub> selectivity with conversion level) can be explained by various secondary reactions of olefins. During the past 20 years, only few researchers have critically questioned the importance of secondary reactions of 1-olefins [6,15–19]. One of the main arguments against the olefin readsorption concept was that it required a majority of in situ-formed olefins to readsorb [8,9], while experiments with externally added olefins showed hydrogenation to be the dominant secondary reaction [9,20–23]. Botes [15] argued that Fe-based catalysts exhibit a lower activity for secondary reactions of olefins [16,24], negating the olefin readsorption explanation for non-ASF distribution of that catalyst, and proposed an alternative theory based on chain length-dependent desorption of olefins. Similar ideas on higher hydrocarbon adsorption with increased chain length can be found in earlier literature

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