

ABSTRACT

Recently, engineers have devoted a great deal of research to developing a Fischer–Tropsch synthesis (FTS) process with high carbon utilization efficiency and low CO₂ emissions. This is desirable not only to improve the process and make it more economical, but also to promote its industrial sustainability. Because CO₂ is produced in both syngas preparation and the FTS step, it may be a significant component in the syngas or in the FT tailgas that may be recycled back to the FT reactor. With the aim of providing new insights into the process that would help engineers to design FT plants with high overall carbon utilization efficiency, we investigated FTS using CO₂-containing syngas mixtures over cobalt- and iron-based catalysts.

During the course of our research, we conducted a large number of experiments on CO/H₂, CO₂/H₂ and CO/CO₂/H₂ syngas mixtures for FTS under different reaction conditions over both cobalt- and iron-based catalysts. The results elicited the following information:

- No apparent catalyst deactivation was observed when we co-fed CO₂ into the feeds during FTS over both cobalt- and iron-based catalysts under the reaction conditions we conducted.
- The rate of hydrocarbon production was maximized at an intermediate composition of the CO/CO₂/H₂ mixtures for a cobalt-based catalyst. The hydrocarbon product formation rate reached a maximum and then maintained this value, even at a high concentration of CO₂ in the H₂/CO/CO₂ feed, over an iron-based catalyst.
- Most of the products for CO₂-rich syngas were short chain paraffins with high CH₄ selectivity and high molar paraffin to olefin (P/O) ratios. The product distribution followed a typical one-alpha Anderson–Schulz–Flory (ASF)

distribution with low alpha values with carbon number $n > 2$. C_2 selectivity lay on or close to the ASF distribution line. However, CH_4 selectivity was far above the line.

- For CO-rich feeds, the product composition shifted to an FT-type product (mainly long chain hydrocarbons) with a low P/O ratio, and followed a two-alpha ASF distribution with high alpha values for carbon number $n > 3$. Furthermore the composition of C_2 was plotted below the ASF distribution line, while for CH_4 was above it.
- The growth factor for paraffins was always higher than that for olefins under the same reaction conditions.
- Although the product selectivity and P/O ratio for FTS were strongly dependent on the operating conditions, the experimental evidence showed that a linear relationship between $P_{(n+1)}/O_{(n+1)}$ and $P_{(n)}/O_{(n)}$ holds for a large number of experiments, independent of the type of the reactor, the composition of the syngas, the reaction conditions and the kind of catalyst.

We used a number of simple models to analyze the experimental data. First we introduced quasi thermodynamic equilibrium assumptions to explain the olefin and paraffin distribution of each of three adjacent olefins ($O_{(n-1)}$, $O_{(n)}$, and $O_{(n+1)}$) and paraffins ($P_{r,(n-1)}$, $P_{r,(n)}$ and $P_{r,(n+1)}$). These were found to describe the deviations from ASF distribution in the C_1 and C_2 components successfully.

We then developed a simple means, called “the combined paraffin and olefin growth factors distribution model”, to explain the two-alpha ASF distribution. This model indicated that a two-alpha product distribution may be the result of the combination of different product spectrums. Another aspect of product distribution that we considered and discussed was the effect of vapour–liquid equilibrium (VLE). This led to our proposing that the deviations from the ASF

distribution we had observed could be explained as the co-action of the different product spectrums (for olefin and paraffin) and the VLE on product distribution during FTS.

In an attempt to explain the linear relationship between $P_{(n+1)}/O_{(n+1)}$ and $P_{(n)}/O_{(n)}$ we had encountered in the experiments, we considered an equilibrium hypothesis. Using a simple VLE model, we found that the ratio of $P_{(n+1)}/O_{(n+1)}$ to $P_{(n)}/O_{(n)}$ changes in a range of $(1, 1/\beta)$, where β is the variation of the vapour pressure coefficient. Our experimental results supported the expression when the chain length was $n > 2$, but with a chain length of $n = 2$, we discovered that it was unable to explain the relationship between P_3/O_3 and P_2/O_2 . Another model, based on quasi reaction equilibrium, was developed to explain the linear relationship between $P_{(n+1)}/O_{(n+1)}$ and $P_{(n)}/O_{(n)}$. We assumed that the reaction of $C_{(n+1)}H_{(2n+2)} + C_{(n)}H_{(2n+2)} = C_{(n+1)}H_{(2n+4)} + C_{(n)}H_{(2n)}$ reaches quasi-equilibrium. Because a comparison between the experimental results and the calculations arising from the equilibrium model showed fairly good agreement, we postulate that the product distribution might be determined by the reaction equilibrium.

Although we could not explain all the questions raised by our experimental results, we must emphasize that the long term effect of the CO_2 on the deactivation of both cobalt- and iron-based catalysts was very small under the reaction conditions we selected. It is thus possible to use CO_2 -containing syngases for FT synthesis with both cobalt- and iron-based catalysts. Therefore, it may not be necessary to remove CO_2 from the raw syngas for FTS. The results could have implications for the design of FT processes using cobalt and iron catalysts.