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On the Growth of Hydrocarbon Chains in the Fischer–Tropsch Synthesis

Comprehension of growth processes by which hydrocarbon chains are formed on the catalyst surface is an important key for improving product selectivity of the Fischer–Tropsch synthesis. Though there is controversy (*1–6*) regarding the surface intermediates and the detailed mechanism involved in the synthesis, it is generally agreed that growth occurs predominantly by a stepwise addition of units containing one carbon atom and that this growth process is analogous to catalyzed polymerization reactions.

In 1946, Herington (*7*) suggested the use of a quantity β_n in the Fischer–Tropsch synthesis, where β_n is the ratio of chain termination (r_t) to chain propagation (r_p) rates. This ratio thus defines the probability of obtaining a hydrocarbon chain of length n in the product to the probability (α_n) of its remaining on the catalyst, adding another C_1 fragment and growing further. Thus,

$$\beta_n = \frac{r_t}{r_p} = \frac{1-\alpha_n}{\alpha_n} = \phi_n / \sum_{n+1}^{\infty} \phi_i, \quad (1)$$

where ϕ_n is the number of moles of product C_n. Friedel and Anderson (*8*) noted that if β_n, and therefore α_n, was constant over any product range beyond any particular value of n equal to x, then from Eq. (1)

$$\phi_n = \alpha\phi_{n-x}. \quad (2)$$

Equation (2) may be solved readily to give

$$\phi_n = \phi_x\alpha^{n-x}. \quad (3)$$

Hence for data fitting Eq. 3, a plot of $\ln\phi_n$ versus n should be linear. Anderson (*9*) demonstrated the applicability of Eq. (3) by using it successfully to analyze data from iron-based catalysts used in the Schwarzheide tests and from several precipitated cobalt–thoria–kieselguhr catalysts.

Anderson *et al.* (*10*) further developed Eq. (3) to take isomer distributions into account by introducing a constant f which was an index of the extent of branching of hydrocarbon chains; where f is the ratio of the rate of appearance of C_n upon addition to an adjacent-to-end carbon of C_{n-1} to the rate of appearance of C_n upon addition to the end carbon of C_{n-1}. The authors postulated that growth could occur by addition at only one end of the growing chain on only one end carbon if two were present or on the adjacent-to-end carbon, with the restriction that quaternary carbon compounds did not form. It was also assumed that both carbon atoms of the C_2 intermediate were effective in end-carbon addition. The authors (*10*) obtained

$$\phi_n = 2\phi_2 g_n(f)\alpha^{n-2}, \quad (4)$$

where $g_n(f)$ is a function only of f, and generally increases slowly with carbon number. Anderson *et al.* (*10*) showed that several data on iron-based and cobalt-based catalysts could be made to fit Eq. (4). Equations (3) and (4) are important, as they help to organize much experimental data in a useful form and allow the determination of the probability of chain growth α.

Assuming that the monomer unit has the

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same molecular weight regardless of position in the growing chain, the weight fraction W_n may be obtained by multiplying Eq. (3) by n and dividing it by $\sum_{n=1}^{\infty} n\phi_n$. If x is put equal to 1, in Eq. (3)

$$W_n = n\phi_n / \sum_{n=1}^{\infty} n\phi_n = n\phi_1\alpha^{n-1} / \sum_{n=1}^{\infty} n\phi_1\alpha^{n-1}$$

$$= n\alpha^{n-1} \Big/ \frac{\partial}{\partial \alpha} \sum_{n=0}^{\infty} \alpha^n$$

$$= n\alpha^{n-1} \Big/ \frac{\partial}{\partial \alpha} (1 - \alpha)^{-1}$$

or

$$W_n = n\alpha^{n-1}(1 - \alpha)^2. \qquad (5)$$

The same result is obtained from Eq. (4), if isomer distribution is not taken into account, in which case f is equal to zero and $g_n(f)$ is therefore equal to 1 (*11*).

Equation (5) was developed in 1936 by Flory (*12*) and in a slightly modified but equivalent form by Schulz (*13*) to explain molecular weight distributions in polymerization. Recently (*5*), the Schulz–Flory Eq. 5 has been used to analyze past Fischer–Tropsch data on cobalt and iron catalysts. But as shown above, this was already demonstrated in detail by Anderson and co-workers more than two decades ago; the equation developed and used by Friedel and Anderson (*8*) being exactly equivalent to the Schulz–Flory distribution law.

Thus, the fact that the Fischer–Tropsch data on past catalysts fit the polymerization distribution law is well known; however, an important ramification of this fact needs to be examined. If indeed the distribution function is obeyed, the maximum weight fraction of a hydrocarbon product C_n, where $n \geq 2$, is fixed and determined by

$$W_{n,\max} = 4n \frac{(n-1)^{n-1}}{(n+1)^{n+1}}, \qquad (6)$$

and this is shown in Fig. 1. The optimal weight fraction of a particular range of hydrocarbon chains, C_i to C_j, is thus fixed

$$\sum_{n=i}^{j} W_n = \sum_{n=i}^{j} n\alpha^{n-1}(1 - \alpha)^2. \qquad (7)$$

Graphical examples of the relationship between the optimal weight fractions and α are given elsewhere (*14*). Thus, the polymerization distribution model sets well-defined limits to the hydrocarbon product selectivity.

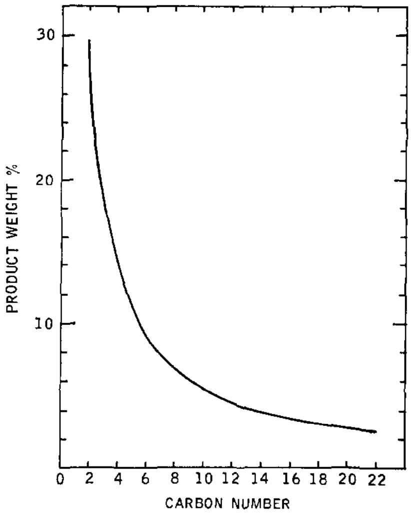

FIG. 1. Maximum product weight percent as predicted by Eq. (6).

An interesting product distribution was observed recently (*15*) on reacting $2H_2$:CO at 3.1 MPa over 1% Ru supported on 60 to 140 mesh γ-Al_2O_3. Experimental details have been given elsewhere (*15*), where the insignificance of transport effects has also been discussed. Figure 2 shows the striking discrepancy between the experimental data (curve A) and the theoretical distribution (curve B) maximized for C_{10} hydrocarbons; 99 wt% of the observed product is between C_5 and C_{25} with negligible gaseous products or wax. Thus the simple polymerization model described by Eq. (3) or (5) does not apply to the data for the Ru/Al_2O_3 catalyst. This suggests that one is not necessarily limited, during Fischer–Tropsch synthesis, to distributions predicted by Eq. (7).

Herington (*16, 17*) has shown how product distributions can depend on termination mechanisms and the variation of β with chain length. Data plotted in semilogarithmic form using Eq. (3) or (5) often tend to mask information regarding subtle variations in catalyst behavior, e.g., small changes in growth patterns may not be easily differentiated with such plots. A better way (*7, 8*) of comparing and perhaps understanding how different catalysts and promoters effect product distributions would be to plot the experimentally determined quantity β_n or α_n as given in Eq. (1) against the carbon number, Fig. 3. The figure delineates the trends of the propagation and termination rates with carbon number. Complete reversal of trend occurs, not at the maximum of the product distribution C_{10}, but at a higher carbon number of C_{16} and again at C_{22}. However, as seen on the α_n plot, a subtle change from the initial trend does occur at C_{10}. Modern chromatographic techniques would allow such plots to be made over the complete range of carbon numbers in the product.

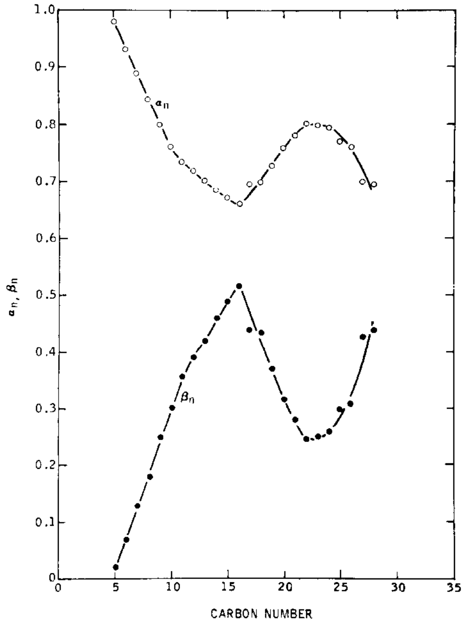

FIG. 3. α_n, β_n versus carbon number.

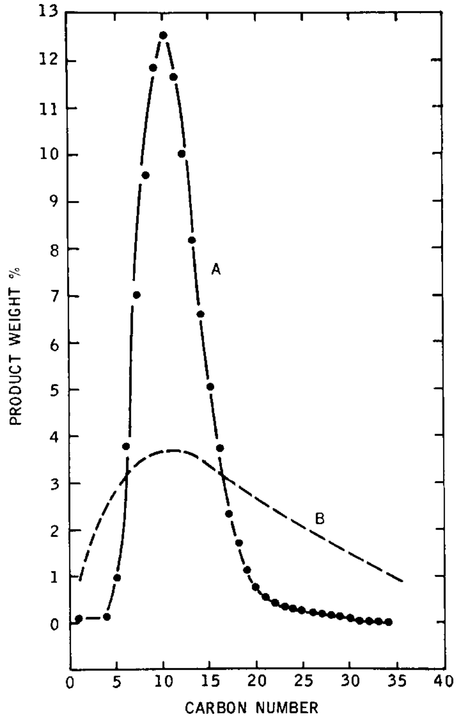

FIG. 2. Comparison of the product distribution (Curve A) obtained over 1% Ru/γ-Al_2O_3 at 241°C, 3.1 MPa, space velocity = 193 V/V/h, and $2H_2$:CO ratio (*15*) with the theoretical distribution (Curve B) obtained from Eq. (5).

An attempt at addressing the problem of product selectivity may be made by carrying the extensive past work of Anderson, Friedel, and others a step further, and questioning how akin the synthesis reaction on different catalytic surfaces, giving products usually less than C_{40}, and traditional polymerization processes, with products usually greater than C_{1000}, really are.

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