

Secondary Effects in the Fischer–Tropsch Synthesis

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α -Olefins, which are primary Fischer–Tropsch products, are known to participate in secondary reactions during the synthesis process. Thus, these α -olefins may readsorb and initiate new hydrocarbon chains, and this may be an important route that decides the overall distribution of products. The analysis for a continuous stirred tank reactor shows that with such a secondary reaction the products still follow a Flory type of distribution. For a plug flow reactor, the distribution deviates from the Flory model if most of the readsorbed α -olefins participate in growth. If, however, as in a more real situation, they also participate in hydrogenation and isomerization reactions, then the distribution rapidly becomes similar to the Flory distribution. Finally, a case where the chain growth parameter, which is normally assumed to be constant, is varied along the length of an isothermal plug-flow reactor by forcing the C_1 surface intermediate concentration to vary is analyzed. The overall product distribution, in such a case, is still quite close to a Flory distribution.

INTRODUCTION

The Fischer–Tropsch (FT) synthesis is a process in which aliphatic hydrocarbons are formed by reacting CO and H₂ on a solid catalyst. Hydrocarbon formation takes place (1) by the addition of a single carbon intermediate to a growing chain. Furthermore, if the chain propagation and termination rates are independent of chain length, and if termination takes place either by desorption or by simple chain transfer, the product distribution has been shown by Friedel and Anderson (2) to fit a most probable distribution which may be represented by

$$\phi_n = \phi_{n_0} \alpha^{n-n_0}, \quad (1)$$

where ϕ_n is the number of moles of product of carbon number n , and α is the chain growth probability. Note that Eq. (1) describes the distribution only for carbon

numbers above C_{n_0} . However, if the minimum carbon number for which the above equation is valid is $n_0 = 1$, then Eq. (1) is equivalent to the Flory equation (3)

$$\begin{aligned} \text{weight fraction } [W_n] &= n\phi_n / \sum_{n=1}^{\infty} n\phi_n \quad (2) \\ &= n(1 - \alpha)^2 \alpha^{n-1}, \end{aligned}$$

which has been used more recently to fit FT data.

Besides fitting their overall product distribution results, as stated above, Friedel and Anderson (2) used thermodynamic equilibrium arguments to suggest that α -olefins were primary FT products. Pichler and co-workers (4, 5) substantiated this suggestion experimentally, proving that paraffins and internal olefins were secondary FT products formed from the primary α -olefins.

Labeled α -olefins have been added to CO and H₂ in the past (6–10) to investigate chain initiation and growth during FT synthesis. More recently Pichler *et al.* (5) and Schulz *et al.* (11) have used labeled α -olefins to investigate secondary reactions. Possible secondary reactions with α -olefins are (i) hydrogenation to give n -paraffins, (ii) isomerization, both skeletal and double-

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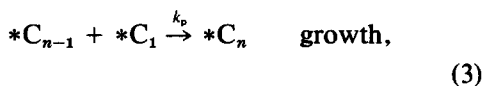
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bond shift, (iii) cracking and hydrogenolysis, (iv) insertion into growing chains, and (v) readsorption and initiation of hydrocarbon chains. Reactions (i) and (ii) are usually most prevalent, and reaction (iv) is probably most effective for C_2H_4 and C_3H_6 . Schulz *et al.* (11) found that reaction (v) took place with both Co and Fe catalysts and stated that such secondary olefin buildup reactions may play an important role during synthesis. Most recently Dwyer and Somorjai (12) echoed a similar opinion in proposing that readsorption and growth of primary α -olefins were an essential route for forming large-molecular-weight hydrocarbons.

Just as we have previously (13) discussed the effect of cracking, we discuss in this paper the effect of readsorption and further growth of primary α -olefins on the overall FT product distribution, and check how much, if any, deviation there is from the standard Flory distribution. The analysis also includes a more real situation in which secondary reactions (i) and (ii) occur in conjunction with reaction (v). Furthermore, as secondary reactions are affected by residence time and by mixing in reactions, the analysis has been performed for both a continuous stirred tank reactor and a plug flow reactor. Finally, we have also considered the effect of the longitudinal variation of α in an isothermal plug flow reactor.

1. SECONDARY REACTIONS

In the absence of secondary reactions, chain growth and termination steps may be simply shown as



where * corresponds to a catalytic site, and k_p and k_t are rate constants for growth and termination, respectively. Let θ_n be the fraction of C_n on the catalyst surface, and let ρ_n be the molar concentration of C_n α -

olefin product divided by the moles of active sites per unit volume of catalyst. Thus both θ_n and ρ_n are dimensionless. The equations that describe the formation of C_n are given by

$$\frac{\partial \theta_n}{\partial t} = k_p \theta_1 \theta_{n-1} - k_p \theta_1 \theta_n - k_t \theta_n, \quad (4a)$$

$$\frac{\partial \rho_n}{\partial t} + \nabla \cdot (\rho_n \mathbf{v}) = k_t \theta_n, \quad (4b)$$

where \mathbf{v} is the velocity of the product C_n leaving the reactor, and θ_1 is the concentration of the C_1 intermediate. Equation (4a) describes the process shown in Eq. (3), and Eq. (4b) is the equation of continuity for products C_n . When the right-hand side of Eq. (4b) is zero, then the concentration of C_n product is a conserved quantity. The term $k_t \theta_n$ is the rate at which the product concentration of C_n is increased as a result of C_n desorbing from the surface as product. At steady state, $\partial \theta_n / \partial t = \partial \rho_n / \partial t = 0$. Assuming steady-state conditions and assuming that the rate constants and θ_1 are independent of position, Eqs. (4a) and (4b) can be readily solved to give Eq. (2), the Flory distribution.

In order to study the effect of secondary reactions, let us now allow some of the primary α -olefin product ρ_n to readsorb with a rate constant k_r . Of the readsorbed α -olefins, assume that some are converted to the corresponding paraffins and isomers with a probability λ , while the remainder initiate and grow longer hydrocarbon chains with a probability $1 - \lambda$. We assume in our analysis that readsorption and secondary reactions of α -olefins are independent of chain length. Also, the secondary reactions, hydrogenation and isomerization, have been grouped together because both reactions only convert one species of C_n into another species that does not undergo further secondary reactions, and we are only interested in the overall product distribution. Finally, we define two quantities μ and μ' having the dimensions of rate constants that describe the physical removal from the reactor of α -olefins, and of paraffins and iso-

mers, respectively. Thus, a more general form of Eq. (4a) and (4b) may be written as

$$\frac{\partial \theta_n}{\partial t} = k_p \theta_1 \theta_{n-1} - k_p \theta_1 \theta_n - k_t \theta_n + (1 - \lambda) k_r \rho_n, \quad (5a)$$

$$\frac{\partial \rho_n}{\partial t} + \nabla \cdot (\rho_n \mathbf{v}) = k_t \theta_n - k_r \rho_n - \mu \rho_n, \quad (5b)$$

$$\frac{\partial \rho'_n}{\partial t} + \nabla \cdot (\rho'_n \mathbf{v}) = \lambda k_r \rho_n - \mu' \rho'_n, \quad (5c)$$

where ρ_n , as before, is the dimensionless molar concentration of α -olefin product with carbon number n while ρ'_n is the dimensionless molar concentration of the corresponding paraffins and isomerized products with carbon number n . The above equations are locally valid; therefore, at this point, any of the above quantities may be considered functions of position (or even of time).

Generally, there may be additional effects that change the population of surface and product species. For example, in addition to terminating as a hydrocarbon product, the surface species may terminate as an alcohol. Though this would diminish the surface concentration of C_n , it would not result in an increase in ρ_n or ρ'_n which describe only the α -olefin and paraffin/isomer product concentrations, respectively. In this paper we do not consider such effects, nor do we consider secondary effects such as hydrogenolysis or the direct insertion of α -olefins into growing chains.

1.1. The Continuous Stirred Tank Reactor

In a continuous stirred tank reactor (CSTR), mixing is complete so that the concentrations of the reaction mixture at all points in the reactor and in the exit stream are identical. The invariance of composition with position allows us to treat the system as a lumped-parameter unit; thus $\nabla \cdot (\rho_n \mathbf{v}) = 0$. At this point, we will analyze the case in which the only secondary reaction that takes place after readsorption of α -olefins is chain initiation and growth, i.e.,

we have $\lambda = \rho'_n = 0$ in Eq. (5). At steady state, $\partial \theta_n / \partial t = \partial \rho_n / \partial t = 0$, and Eq. (5) becomes

$$0 = k_p \theta_1 \theta_{n-1} - k_p \theta_1 \theta_n - k_t \theta_n + k_r \rho_n, \quad (6a)$$

$$0 = k_t \theta_n - k_r \rho_n - \mu \rho_n. \quad (6b)$$

Note that $\mu \rho_n$ accounts for the physical removal of C_n from the reactor and conserves the overall material balance.

From Eq. (6b)

$$\rho_n = \frac{k_t}{k_r + \mu} \theta_n. \quad (7)$$

On substituting for ρ_n in Eq. (6a),

$$0 = k_p \theta_1 \theta_{n-1} - k_p \theta_1 \theta_n - k_t \theta_n + \frac{k_r k_t}{k_r + \mu} \theta_n. \quad (8)$$

This is analogous to Eq. (4a) at steady state from which the Flory equation (Eq. (2)) is derived, except that here we have a smaller effective termination rate constant given by

$$k_t - k_r \frac{k_t}{k_r + \mu}. \quad (9)$$

Thus, the effect of readsorption should be to favor heavier product make. Before showing this, we introduce the parameters

$$\alpha = \frac{k_p \theta_1}{k_p \theta_1 + k_t}, \quad (10)$$

$$q = \frac{k_r}{\mu}, \quad (11)$$

where α is the growth probability of a hydrocarbon chain in the absence of readsorption (see Eq. (2)), and q measures the probability of readsorbing any C_n product as opposed to removing it from the system. The actual probability of readsorption is $q / (1 + q)$. Equation (8) may now be rewritten as

$$0 = \alpha \theta_{n-1} - \theta_n + \frac{q}{1 + q} (1 - \alpha) \theta_n. \quad (12)$$

The solution to Eq. (12) gives a distribution that is analogous to a Flory distribution. We have

$$\theta_n = \bar{\alpha}^{n-1} \theta_1, \quad n \geq 2, \quad (13)$$

with an effective α given by

$$\bar{\alpha} = \frac{\alpha}{1 - [q/(1+q)](1-\alpha)}. \quad (14)$$

The weight fraction of C_n product is

$$W_n = \frac{n\rho_n}{\sum_{n=1}^{\infty} n\rho_n}. \quad (15)$$

Equations (7) and (13) determine ρ_n in terms of the parameters for $n \geq 2$. However, ρ_1 must be treated as a special case. Although a fraction of C_{2+} products, being α -olefins, can readsorb, one cannot similarly assume that CH_4 readsorbs; therefore, setting $k_r = 0$ and $n = 1$ in Eq. (6b) gives

$$\rho_1 = \frac{k_t}{\mu} \theta_1. \quad (16)$$

From Eqs. (7), (13), (15), and (16)

$$W_1 = \frac{q+1}{q + [1/(1-\bar{\alpha})^2]}, \quad (17)$$

$$W_n = \frac{n\bar{\alpha}^{n-1}}{q + [1/(1-\bar{\alpha})^2]}, \quad n \geq 2.$$

Figure 1 shows the effect of increasing the readsorption rate relative to the rate of product removal for α fixed at 0.6. As indicated, α -olefin readsorption and growth favor heavier product make. The high methane levels observed in the product

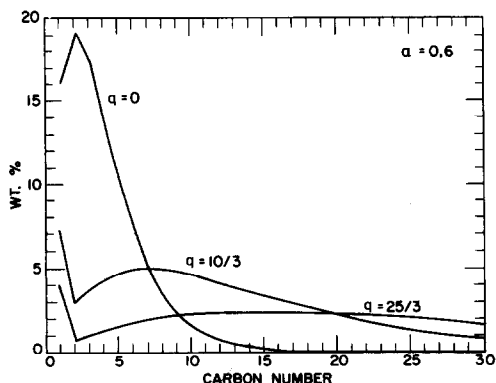


FIG. 1. Product distributions in a CSTR, α is fixed at 0.6. As q is increased, the distribution shifts to give heavier products.

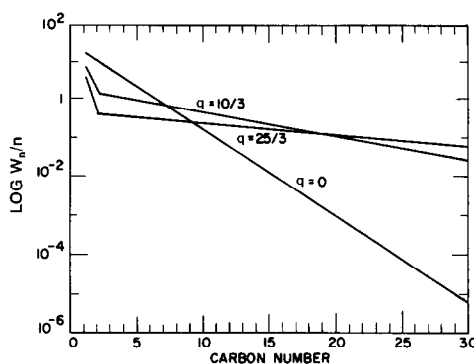


FIG. 2. Readsorption and growth of primary α -olefin products in a CSTR does not change the shape of the product distribution from a Flory distribution for C_{2+} products. Parameters are the same as in Fig. 1.

distribution for $q \neq 0$ result because CH_4 , unlike the C_{2+} α -olefins, does not readsorb and participate in further chain growth. It should be noted that the distributions are Flory-like for C_2^2 . This may be seen from the semilogarithmic plots in Fig. 2. For a Flory distribution $\log W_n/n$ varies linearly with n . Figure 2 indicates no departure from a linear variation except for CH_4 .

In the more general case in which $\lambda \neq 0$, α -olefins may readsorb and hydrogenate and/or isomerize. Hence, fewer α -olefins are available to participate in chain growth. As a result, the shift in the product distribution to heavier product make is not as pronounced. The distribution is still Flory-like and is also described by Eq. (17) but with $\bar{\alpha}$:

$$\bar{\alpha} = \frac{k_p \theta_1}{k_p \theta_1 + \left[1 - \frac{(1-\lambda)k_r}{k_r + \mu} \right] k_t}. \quad (18)$$

1.2. The Plug Flow Reactor

In a plug flow reactor (PFR), the concentration of the reaction mixture varies along the length of the reactor tube, and the effluent composition is thus an overall integral composition. Unlike a CSTR, the PFR is a distributed parameter system: $\nabla \cdot (\rho_n \mathbf{v}) \neq 0$.

In order to disregard the mathematical complexities associated with two-phase flow, we assume that all of the product output is in a single phase, either gas or liquid.

Furthermore, we assume that the product moves at a constant velocity v , which is independent of the product position along the reactor tube. Though these assumptions constitute an oversimplification, they at least allow us to qualitatively determine the effect of α -olefin readsorption and subsequent growth in a PFR, and compare the results with those in a CSTR. Finally, it is possible that the Flory chain growth probability α (defined in Eq. (10)) may also vary along the length of the reactor. However, as we will concern ourselves only with an isothermal system, all rate constants may be assumed to be invariant with position. Also, in the next section, we show that when θ_1 is allowed to vary with reactor length, the resultant product distribution does not deviate substantially from the Flory distribution. Anticipating this result, we believe that allowing θ_1 to vary with position, while greatly increasing the complexity of the present model, would not constitute a major correction to the final solution. Therefore, θ_1 and hence α will be assumed to be independent of position.

Let x be the position along the reactor tube, with $x = 0$ at the reactor inlet and $x = L$ at the outlet. θ_n and ρ_n are now functions of x . Assuming steady-state conditions and assuming for the present that $\lambda = \rho' = 0$, we obtain from Eq. (5)

$$0 = k_p \theta_1 \theta_{n-1}(x) - k_p \theta_1 \theta_n(x) - k_t \theta_n(x) + k_r \rho_n(x), \quad (19a)$$

$$\frac{v \partial \rho_n(x)}{\partial x} = k_t \theta_n(x) - k_r \rho_n(x). \quad (19b)$$

These equations are similar to Eq. (6), except that in the PFR the term $v \partial \rho_n(x) / \partial x$ replaces $\mu \rho_n$ and takes into account the local removal of products.

The solution of Eqs. (19a) and (19b) is outlined in Appendix A. The observed product distribution is that measured at the end of the reactor and is, therefore, $\rho_n(L)$. It is convenient to express $\rho_n(L)$ in terms of the Flory α and the readsorption parameter q . For the PFR,

$$q = \frac{k_r L}{v}. \quad (20)$$

The quantity v/L has the dimensions of a rate constant, and may be looked upon as a space velocity. Therefore, q measures the probability that C_n will be readsorbed as opposed to being carried downstream. In terms of the above parameters,

$$\rho_1(L) = \frac{k_t L}{v} \theta_1, \quad (21)$$

$$\rho_n(L) = \frac{k_t L}{v} \alpha^{n-1} \theta_1 e^{-\alpha q} \sum_{j=0}^{n-2} \frac{(n-2)!(1/\alpha-1)^j}{(n-2-j)!j!} \sum_{l=j+1}^{\infty} \frac{1}{l!} (\alpha q)^{l-1}.$$

The total weight of C_n product output can then be determined from Eq. (21) to be proportional to

$$W_T \propto \sum_{n=1}^{\infty} n \rho_n = \frac{k_t L}{v} \frac{[1 + (\alpha^2/2)q]}{(1-\alpha)^2} \theta_1. \quad (22)$$

Therefore, from Eqs. (21) and (22) the observed weight fraction W_n of C_n product is given by

$$W_1 = \frac{(1-\alpha)^2}{1 + (\alpha^2 q/2)}, \quad (23)$$

$$W_n = \frac{n \alpha^{n-1} (1-\alpha)^2}{1 + (\alpha^2 q/2)} e^{-\alpha q} \sum_{j=0}^{n-2} \frac{(n-2)!(1/\alpha-1)^j}{(n-2-j)!j!} \sum_{l=j+1}^{\infty} \frac{1}{l!} (\alpha q)^{l-1},$$

$n \geq 2.$

Note that to zeroth order in q , only the $j = 0$ and $l = 1$ terms contribute to W_n in Eq. (23). Therefore, in the limit $q \rightarrow 0$, that is, when the readsorption rate constant is very small compared to the space velocity, Eq. (23) reduces to a Flory distribution. The readsorption effect should begin to be significant when $q \sim 1/\alpha$. This implies that it becomes important when

$$\frac{v}{L} < \alpha k_r. \quad (24)$$

Figure 3 shows the effect of increasing the readsorption rate constant relative to

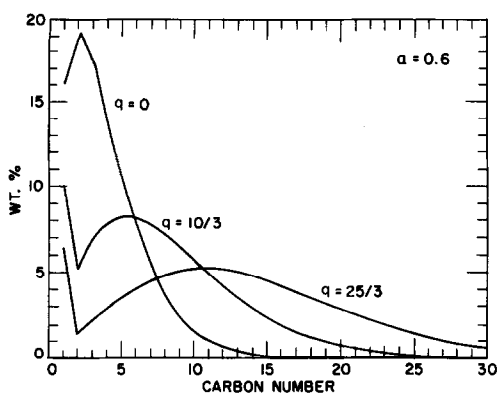


Fig. 3. Product distributions in a PFR. Note that the shift in the distribution to heavier products is not as pronounced as for a CSTR (Fig. 1).

the space velocity. The high methane levels observed in the product distributions may again be attributed to the fact that methane does not readsorb and participate in further chain growth. Using the same values of the parameters as were used previously for a CSTR, one finds that the shift in the distribution toward heavier product make is not as pronounced for a PFR. This is in accord with the known behavior of CSTR and PFR for consecutive reactions (14).

The more interesting effect of product readsorption in a flow reactor is indicated in Fig. 4, where it is shown that the distributions differ in shape from the Flory-like distributions obtained in a CSTR. The plots of

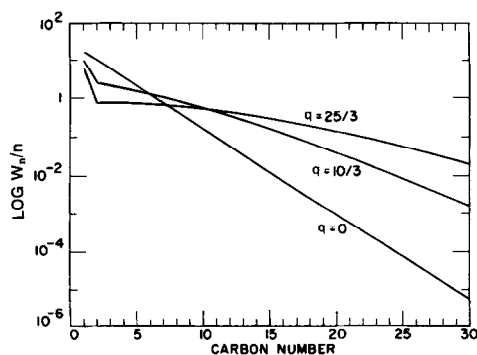


Fig. 4. Readsorption and growth of primary α -olefin products in a PFR changes the shape of the product distribution from a Flory distribution as indicated by the nonlinear dependence of $\log W_n/n$ vs n . Parameters are the same as in Fig. 3.

$\log W_n/n$ vs n clearly deviate from the straight lines characteristic of Flory distributions.

This is consistent with the kind of behavior one might intuitively expect. Due to readsorption the probability of growing longer chains would increase with x . The shorter chains, favored at the beginning of the reactor, would be able to readsorb over distances comparable to the length of the reactor, thereby depleting the supply of shorter chains relative to the total output. On the other hand, if readsorption and growth are an important path for chain formation, the very longest chains would be produced in a significant amount at the end of the reactor, and hence, could not appreciably contribute to the total product output either. The net effect would be to increase the relative amount of chains of intermediate length, thereby increasing the selectivity of the distribution as compared to a Flory distribution.

Figure 5 shows the effect of increasing the readsorption probability while keeping the peak position, carbon number n_p fixed at $n_p = 8$. The parameter α is adjusted to keep n_p fixed. For the three values of q (zero, 3.3, and 5.6) indicated in the figure the corresponding α values are 0.88, 0.70, and 0.60, respectively. As suggested by Fig. 4, the distributions are more selective

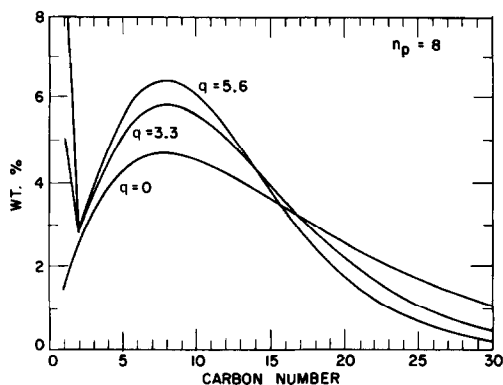


Fig. 5. Product distributions for different values of q . Increasing the readsorption rate constant relative to the space velocity while keeping the peak fixed at $n_p = 8$ increases the selectivity of the process in a PFR.

than Flory distributions, and increasing the readsorption parameter increases the selectivity.

So far we have assumed $\lambda = 0$. When $\lambda = 1$, the α -olefin primary product readsorbs and hydrogenates and/or isomerizes but does not participate in chain growth. Since one species of C_n is simply being converted to another species of C_n without changing the total amount of C_n , the product distribution will be identical to the Flory distribution.

We now consider the case when both secondary reactions take place, i.e., $0 < \lambda < 1$. The hydrogenation and/or isomerization reactions will serve to deplete the population of adsorbed α -olefins which are available for readsorption and growth. Consequently, these added secondary reactions tend to make the final product distribution more like a Flory distribution.

From Eq. (5) we have

$$0 = k_p \theta_1 \theta_{n-1}(x) - k_p \theta_1 \theta_n(x) - k_t \theta_n(x) + (1 - \lambda) k_r \rho_n(x), \quad (25a)$$

$$\frac{v \partial \rho_n(x)}{\partial x} = k_t \theta_n(x) - k_r \rho_n(x), \quad (25b)$$

$$\frac{v \partial \rho'_n(x)}{\partial x} = \lambda k_r \rho_n(x), \quad (25c)$$

where ρ'_n , as defined previously in Eq. (5), includes both the hydrogenated and isomerized product concentrations. The final product distribution is determined by solving Eq. (25) and substituting the result into

$$W_n = \frac{n(\rho_n + \rho'_n)}{\sum_{n=1}^{\infty} n(\rho_n + \rho'_n)} \quad (26)$$

at $x = L$. The actual form of the solution to Eq. (25), given in Appendix B, is somewhat complex and is of minor importance with regard to the following discussion. The parameters that determine the product distribution are the Flory α , the readsorption parameter q , and the probability λ of hydrogenation and/or isomerization.

In Fig. 6 the readsorption parameter is fixed at $q = 5.63$. The probability of conver-

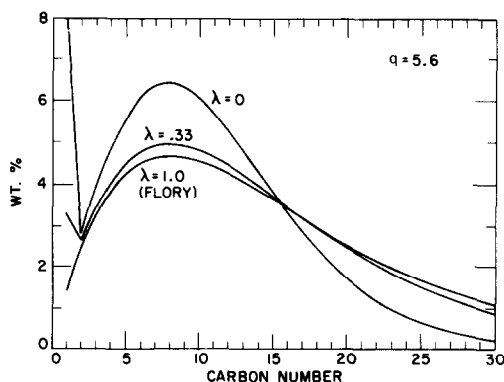


FIG. 6. Product distributions for different values of λ . Increasing the probability of conversion of primary α -olefins to paraffins and/or isomers decreases the effect of readsorption and subsequent growth in altering the shape of the product distribution. For $\lambda = 0$ the distribution is composed entirely of α -olefins; for $\lambda = 0.33$, it is 47% α -olefins and 53% paraffins and/or isomers; for $\lambda = 1$, the distribution follows the Flory distribution and is composed of primary α -olefins, paraffins, and isomers.

sion to secondary products is varied from $\lambda = 1$ to $\lambda = 0$, while the peak of the distribution is fixed at C_8 . When $\lambda = 1$ the distribution, which is a Flory distribution, is composed only of primary α -olefins and secondary paraffinic and isomerized products. When $\lambda = 0$ the distribution is composed entirely of α -olefins. With the readsorption parameter and the peak fixed as indicated above, one finds that a probability $\lambda = 0.33$, for conversion of olefins into secondary products upon readsorption, results in a final product distribution that is 53% hydrogenated and/or isomerized products by weight. Note that this product distribution differs only insignificantly from the Flory distribution at $\lambda = 1$. Increasing λ so that the percentage of hydrogenated and/or isomerized products increases reduces the deviation from the Flory distribution even further. This suggests that if hydrogenated and/or isomerized products constitute a substantial fraction of the final product distribution (on the order of one-half or greater), it is unlikely that the readsorption of primary α -olefins and their subsequent growth effect significant changes in the

shape of the product distribution as compared with a Flory distribution.

2. VARIATION OF THE CHAIN GROWTH PARAMETER α IN A PFR

In the previous section, we investigated the effect of product readsorption and continued growth in FT synthesis. The chain growth parameter, α , as defined by Eq. (10), was assumed to be invariant with position. However, even in the absence of product readsorption, a variation in α alone along the length of a PFR could result in modifying the product distribution from a Flory distribution. Therefore, in this section α is assumed to be a function of x . Readsorption and continued growth of product will be assumed not to occur. This is done both for the sake of simplicity and in order that the effect of changing growth conditions may be investigated independently of the former effect.

It is worthwhile to consider the reaction conditions that could result in a variation in α with x . With increasing x , the H_2 and CO partial pressures decrease, since the reactants are continually being converted into product. Consequently, unless the surface is everywhere close to saturation, independent of x , this may induce changes in the adsorbed reactant concentrations with x . The variations in the reactant surface concentrations may in turn induce a variation in θ_1 , the concentration of the intermediate that is formed from these reactants. Although changes in the rate constants for growth and desorption may also result from changes in the reactant concentrations, we contend, especially since we are dealing with an isothermal system, that the predominant effect on α is the variation of θ_1 with x . It is not clear how the reactant concentrations or θ_1 actually vary with x , since the detailed kinetics of the reaction are unknown. Since a linear variation in θ_1 should induce the most significant change in the product distribution, we confine our subsequent analysis to this case.

The following argument will not depend

on whether θ_1 is linearly increasing or decreasing with x ; however, for the convenience of the discussion, it will hereafter be assumed that θ_1 decreases with x . Then

$$\theta_1 = \theta_1^0 (1 - \beta x), \quad (27)$$

where β is arbitrary and has the dimensions of a reciprocal length.

Under steady-state conditions, Eqs. (4a) and (4b) become

$$0 = k_p \theta_1(x) \theta_{n-1}(x) - k_p \theta_1(x) \theta_n(x) - k_t \theta_n(x), \quad (28)$$

$$\frac{v \partial \rho_n}{\partial x} = k_t \theta_n(x),$$

where θ_1 is a function of x defined by Eq. (27) and v as in Section 1.2 is assumed to be constant. The solution to Eq. (28) is given by

$$\theta_n(x) = \alpha^{n-1}(x) \theta_1(x), \quad (29)$$

$$\rho_n(x) = \frac{k_t}{v} \int_0^x \theta_n(\xi) d\xi.$$

The parameter α is, as before, defined to be

$$\alpha = \frac{k_p \theta_1}{k_p \theta_1 + k_t}. \quad (30)$$

The x dependence of α may be determined by substituting Eq. (27) into the above equation for α .

The resulting weight distribution of products is given by

$$W_n = \frac{n \rho_n(L)}{\sum_{n=1}^{\infty} n \rho_n(L)} = \frac{n \int_0^L \alpha^{n-1}(x) \theta_1(x) dx}{\int_0^L \{1/[1 - \alpha(x)]^2\} \theta_1(x) dx}. \quad (31)$$

Expressing the integrand in terms of α using Eq. (30) and dx in terms of $d\alpha$ using Eqs. (27) and (30), W_n becomes

$$W_n = \frac{12n \int_{\alpha_0}^{\alpha_1} \frac{\alpha^n}{(1 - \alpha)^3} d\alpha}{\frac{4\alpha_1 - 1}{(1 - \alpha_1)^4} - \frac{4\alpha_0 - 1}{(1 - \alpha_0)^4}}, \quad (32)$$

where α_0 is the value of α at $x = 0$, and α_1 is the value of α at $x = L$.

Figure 7 shows that even under extreme conditions where α is allowed to vary from $\alpha_0 = 0$ to $\alpha_1 = 0.9$, the shape of the product distribution does not significantly deviate from a Flory distribution.

DISCUSSION

In a CSTR, the effect of secondary reactions involving the adsorption and further growth of primary α -olefins is to give product distributions that cannot be differentiated from the Flory distribution. In essence, such secondary reactions decrease the termination rate, the Flory α being modified as shown in Eqs. (14) and (18), and a heavier product distribution is obtained. Though there is a deviation in the CH_4 make (Fig. 2), the fact that it falls above the line in the $\log W_n/n$ vs n plot cannot be assumed to indicate that the above-mentioned secondary reactions are dominating during synthesis. Methanation need not occur at rates that reflect polymerization kinetics. Other secondary reactions like hydrogenolysis can also increase the CH_4 make (11). Differential laboratory flow reactors are in principal identical to the CSTR. Thus when Dwyer and Somorjai

(12), using a differential reactor, added ethylene and propylene to CO and H_2 over Fe, they found that the added olefins reacted during synthesis to give heavier hydrocarbons and that the overall distribution was readily fitted to the Flory equation. Furthermore, they proposed readsorption and secondary reactions of α -olefins to be a major pathway for producing heavy hydrocarbons during FT synthesis.

In addition to readsorption and growth, Schulz *et al.* (11) performed experiments to determine the relative importance of various other secondary reactions. They found, for example, that of the ^{14}C -tagged propylene added during FT synthesis on a Co catalyst, 93% reacted: 54% was hydrogenated and 33% took part in further growth. On Fe, 44% of the added propylene reacted, of which 95% was hydrogenated and only 2.5% took part in growth. Comparing the results of our model for a PFR (Fig. 6) with the above experimental results, we assume that 85% (i.e., $q/(1+q)$, where $q = 5.6$) of the α -olefins react, of which 33% hydrogenate/isomerize and 67% participate in further chain growth. Thus even assuming a relatively low amount of hydrogenation as compared to experiment, we obtain a resulting product distribution that is virtually indistinguishable from a Flory distribution. This suggests that even though readsorption and growth can effectively change the shape of the product distribution (Fig. 5), in practice one should obtain distributions from a PFR that are essentially Flory distributions.

Finally, even if the chain growth probability α is forced to vary substantially along an isothermal PFR due to variation in the C_1 surface intermediate concentration, the overall product distribution is still quite close to the Flory distribution.

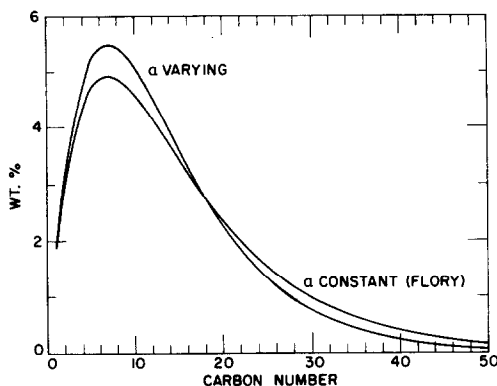


FIG. 7. Product distributions for constant (Flory) and varying values of the chain growth parameter α in an isothermal PFR. In the latter case α has been allowed to vary from 0 at the reactor inlet to 0.9 at the outlet. The difference between the two distributions is small.

APPENDIX A: SOLUTION TO Eq. (19)

We begin by rewriting Eq. (19) as

$$\theta_n(x) = \alpha\theta_{n-1}(x) + k_r(1 - \alpha) \frac{\rho_n(x)}{k_t}, \quad (\text{A1})$$

$$v \frac{\partial \rho_n(x)}{\partial x} + k_r \rho_n(x) = k_t \theta_n(x),$$

where α is the growth probability in the absence of readsorption. The second of the above equations can be solved for $\rho_n(x)$ in terms of $\theta_n(x)$ with the result that

$$\rho_n(x) = \frac{k_t}{v} \int_0^x \theta_n(\xi) e^{(k_r/v)(\xi-x)} d\xi \quad (\text{A2})$$

where we have imposed the boundary condition that $\rho_n(0) = 0$.

When Eq. (A2) is substituted into Eq. (A1) the result is a system of integral difference equations for $\theta_n(x)$:

$$\theta_n(x) = \alpha\theta_{n-1}(x) + \frac{k_r}{v} (1 - \alpha) \int_0^x \theta_n(\xi) e^{(k_r/v)(\xi-x)} d\xi. \quad (\text{A3})$$

Defining

$$\tilde{\theta}_n(p) = \int_0^\infty \theta_n(x) e^{-px} dx. \quad (\text{A4})$$

Equation (A3) may be converted into an ordinary system of difference equations for $\tilde{\theta}_n(p)$ by multiplying Eq. (A3) by e^{-px} and integrating from zero to infinity. Integrating by parts where necessary, one obtains the equation for $\tilde{\theta}_n(p)$:

$$\tilde{\theta}_n(p) = \alpha\tilde{\theta}_{n-1}(p) + (1 - \alpha) \frac{k_r/v}{k_r/v + p} \tilde{\theta}_n(p). \quad (\text{A5})$$

The solution to Eq. (A5) is given by

$$\tilde{\theta}_n(p) = \frac{\theta_1}{p} \frac{\alpha^{n-1}}{\left[1 - \frac{k_r(1-\alpha)/v}{k_r/v + p}\right]^{n-1}}, \quad (\text{A6})$$

where we have made use of the fact that from Eq. (A4) $\tilde{\theta}_1(p) = \theta_1/p$. The solution for $\theta_n(x)$ may then be determined by performing the following integration in the complex plane

$$\theta_n(x) = \frac{1}{2\pi i} \int_{C-i\infty}^{C+i\infty} \tilde{\theta}_n(p) e^{px} dp \quad (\text{A7})$$

with the result that

$$\theta_n(x) = \alpha^{n-1} \theta_1 \left\{ \frac{1}{\alpha^{n-1}} + \frac{1}{(n-2)!} \frac{d^{n-2}}{dp^{n-2}} \left[\frac{(k_r/v + p)^{n-1} e^{px}}{p} \right] \right\}_{p=-\alpha k_r/v} \quad (\text{A8})$$

The first term is the contribution from the first-order pole at $p = 0$, and the second term is the contribution from the $(n-1)$ st-order pole at $p = -\alpha k_r/v$.

In order to obtain the solution for the product $\rho_n(x)$, first define

$$\tilde{\rho}_n(p) = \int_0^\infty \rho_n(x) e^{-px} dx. \quad (\text{A9})$$

Then it follows from Eq. (A2) that

$$\tilde{\rho}_n(p) = \frac{k_t/v}{k_r/v + p} \tilde{\theta}_n(p). \quad (\text{A10})$$

Making use of Eqs. (A6) and (A10) and the fact that

$$\rho_n(x) = \frac{1}{2\pi i} \int_{C+i\infty}^{C-i\infty} \tilde{\rho}_n(p) e^{px} dp, \quad (\text{A11})$$

one obtains the expression for $\rho_n(x)$,

$$\rho_n(x) = \frac{k_t}{v} \alpha^{n-1} \theta_1 \left\{ \frac{1}{\alpha^{n-1}} \frac{1}{k_r/v} + \frac{1}{(n-2)!} \left[\frac{d^{n-2}}{dp^{n-2}} \frac{(k_r/v + p)^{n-2} e^{px}}{p} \right] \right\}_{p=-\alpha k_r/v}. \quad (\text{A12})$$

The observed product output is $\rho_n(L)$. Performing the differentiation indicated in Eq. (A12) and letting $q = k_r L/v$, one finds that

$$\rho_n(x) = \frac{k_t L}{v} \frac{\alpha^{n-1} \theta_1}{q} \left\{ \frac{1}{\alpha^{n-1}} - \frac{e^{-\alpha q}}{\alpha} \sum_{j=0}^{n-2} \frac{(n-2)!(1/\alpha-1)^j}{(n-2-j)!j!} \sum_{l=0}^j \frac{1}{l!} (\alpha q)^l \right\}. \quad (\text{A13})$$

Using the fact that

$$\sum_{l=0}^j \frac{1}{l!} (\alpha q)^l = e^{\alpha q} - \sum_{l=j+1}^{\infty} \frac{1}{l!} (\alpha q)^l. \quad (\text{A14})$$

Equation (A13) simplifies to

$$\rho_n(L) = \frac{k_t L}{v} \alpha^{n-1} \theta_1 e^{-\alpha q} \sum_{j=0}^{n-2} \frac{(n-2)!(1/\alpha-1)^j}{(n-2-j)!j!} \sum_{l=j+1}^{\infty} \frac{1}{l!} (\alpha q)^{l-1}. \quad (\text{A15})$$

APPENDIX B: SOLUTION TO Eq. (25)

Equations (25a) and (25b) are identical to

Eq. (19) except for the factor $(1 - \lambda)$ multiplying the last term in Eq. (25a). Since the method of solution to Eq. (19) is outlined in Appendix A, the solution to Eq. (25) for $\rho_n(L)$, which determines the final distribution of α -olefins, will simply be exhibited here.

$$\begin{aligned} \rho_1(L) &= 0, \\ \rho_n(L) &= \frac{k_t L}{v} \alpha^{n-1} \theta_1 e^{-\bar{\alpha}q} \\ &\sum_{j=0}^{n-2} \frac{(n-2)!(1/\bar{\alpha} - 1)^j}{(n-2-j)!j!} \sum_{l=j+1}^{\infty} \frac{1}{l!} (\bar{\alpha}q)^{l-1}, \\ &n \geq 2, \quad (\text{B1}) \end{aligned}$$

where

$$\bar{\alpha} = 1 - (1 - \lambda)(1 - \alpha). \quad (\text{B2})$$

The distribution of paraffins and/or isomers is determined by integrating $\rho_n(x)$ with respect to x from $x = 0$ to $x = L$ and applying the boundary condition $\rho'_n(0) = 0$. From Eq. (25c), $\rho'_n(L)$ is given by

$$\begin{aligned} \rho'_1(L) &= \frac{k_t L}{v} \theta_1, \\ \rho'_n(L) &= \frac{k_t L}{v} \frac{\lambda}{\bar{\alpha}} \alpha^{n-1} \theta_1 e^{-\bar{\alpha}q} \\ &\sum_{j=0}^{n-2} \frac{(n-2)!(1/\bar{\alpha} - 1)^j}{(n-2-j)!j!} \\ &\sum_{l=j+1}^{\infty} \frac{l-j-1}{l!} (\bar{\alpha}q)^{l-1}, \quad n \geq 2. \quad (\text{B3}) \end{aligned}$$

Finally, the weight fraction of C_n is determined by substituting Eqs. (B1) and (B3) into the equation for W_n :

$$W_n = \frac{n(\rho_n + \rho'_n)}{\sum_{n=1}^{\infty} n(\rho_n + \rho'_n)} \Big|_{x=L}. \quad (\text{B4})$$

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