

Carbon Number Distribution of Fischer-Tropsch Products Formed on an Iron Catalyst in a Slurry Reactor

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Studies at 234 to 269°C and at 790 kPa showed a precise linear relationship between the log of mole fraction m_n of products of carbon number n , and n , as predicted by the Flory molecular-weight distribution provided that all products, including oxygenated species, are considered. The relationship held over more than four orders of magnitude of m_n , values of n of from 1 to about 20, and over a wide range of gas composition. The chain growth probability factor, α , increased slightly from 0.67 at 269°C to 0.71 at 234°C.

A substantial number of papers postulate various mechanisms for chain growth in Fischer-Tropsch synthesis and present the resulting predictions of the distribution of the products. The first attempts to analyze the Fischer-Tropsch product distributions mathematically as a polymerization process that could be treated in terms of relative probabilities appear to be those of Herington (1). He considered n -paraffins and α - and β -olefins and postulated that they were formed by stepwise addition of a methylene radical onto a growing chain on the catalyst surface. The probability β_n that each carbon (C) number will appear as a product in contrast to continuing to grow on the catalyst surface is given by

$$\beta_n = m_n / \sum_{n+1}^{\infty} m_i, \quad (1)$$

where m_n is the mole fraction of carbon number n . Herington experimentally demonstrated that β_n values remained fairly constant at 0.28 for olefins plus paraffins from C_5 to C_{11} formed on a cobalt catalyst. He suggested that much of the CH_4 probably appeared by a different mechanism.

A useful form of Eq. (1) is

$$1 + \beta = m_n / m_{n+1}. \quad (2)$$

Often it is desirable to focus attention on a specific range of hydrocarbons formed. For the mole fraction of m_n relative to the mole fraction of any other carbon number x , m_x , Eq. (3) is readily derived:

$$m_n = m_x (1 + \beta)^{x-n}. \quad (3)$$

Weller and Friedel (2) later proposed a method, also based on probability considerations, by which methyl-substituted isomer distributions for saturated hydrocarbons within any one C number in the range C_5 to C_8 formed on a cobalt catalyst could be correlated. Anderson *et al.* (3) extended this model to include the carbon number distribution. Satisfactory agreement was obtained between theory and experiment for hydrocarbon products from iron or cobalt catalysts. For a stepwise addition of one carbon atom entity to either the terminal or an internal secondary carbon on a growing chain, Anderson and co-workers proposed that

$$m_n = km_2 F_n a^{n-2}, \quad (4)$$

where a and k are constants. Assigning a

different probability to the two types of addition steps, the term F_n increases with C number and equals $[1 + (n - 3)f + (n - 4)(n - 5)f^2/2]$ for $n \geq 4$, neglecting third-order effects which are usually insignificant. Since there are no branched C_2 and C_3 hydrocarbons, F_n is 1 for $n = 2$ or 3. If m_2 is assigned a relative value of 1, then k is 2. The low value at C_2 results from the assumption that, unlike the polymerization process for larger molecules, chain growth can occur on either end of a C_2 group. Equation (4) simplifies to Eq. (3) when $x = 2$ and for $k = 1$ and $f = 0$ in Eq. (4). Then $1 + \beta = 1/a$ and a equals α as defined below.

More recently, Anderson and Chan (4) modified this chain growth sequence by introducing another parameter g to account for ethyl-substituted isomers. By using experimental data reported in the literature, the parameters, a , f , and g were adjusted by computer simulation of the Fischer-Tropsch process to give the best fit. While the general pattern is predicted for C_4 to C_9 isomers, deviations of computed compared to experimental results were much smaller for products formed over a cobalt catalyst than those from an iron catalyst.

Henrici-Olivé and Olivé (5) evaluated Fischer-Tropsch product distributions with an expression derived by Schulz (6) for the radical polymerization of vinyl monomers:

$$w_n = (\ln^2 \alpha) n \alpha^n, \quad (5)$$

where w_n is the weight fraction of hydrocarbon containing n carbon atoms and α is the chain growth probability factor defined as

$$\alpha = r_p / (r_p + r_t), \quad (6)$$

where r_p and r_t are the rates of propagation and termination, respectively.

Their reanalysis of published experimental data for cobalt catalysts showed a good fit for hydrocarbons between C_4 and C_{12} . Deviations of the C_1 to C_3 fractions were attributed to secondary decomposition of ethylene and propylene to methane, and to a smaller degree, to incorporation of these

components back into the growing chains. At the upper end of the distribution, an increasingly poorer fit by the model was suggested to be the result of either hydrocarbon cracking or further polymerization. They also pointed out that discrepancies at high carbon numbers might be due to underestimation by the gas chromatographic technique used in the analysis.

Using a statistical approach, Flory (7) derived the molecular-weight distribution for a linear condensation polymerization. This same mathematical expression has since been shown (see, e.g. (8)) to apply to any polymerization process, regardless of the mechanism, where the primary step is the addition of carbon units one at a time onto the terminus of a growing linear chain, and one polymer molecule is produced from each kinetic chain, i.e., termination by coupling is negligible. The mole fraction m_n of molecules in the polymer mixture which contains n structural units is given by

$$m_n = (1 - \alpha)\alpha^{(n-1)}. \quad (7)$$

In each stage of the polymerization process an equal opportunity for reaction is assumed to be available to each functional group of a given chemical type, irrespective of the size of the molecule to which it is attached. In other words, the probability of chain growth α is taken to be independent of molecular size.

If the added weight of each carbon unit is proportional to chain length n , the weight fraction distribution w_n is

$$w_n = (1 - \alpha)^2 n \alpha^{(n-1)}. \quad (8)$$

At $\alpha > 0.5$, Flory noted that this equation is equivalent to that developed by Schulz (Eq. (5)). However, the greater weight per carbon number of Fischer-Tropsch products with oxygenated end groups cannot be neglected at very low molecular weights and the error introduced by this approximation is significant. For example, over an iron catalyst, in the C_2 fraction a large amount of ethanol is produced together with ethylene and ethane. Little methanol is normally

formed but the greater weight per carbon number for CH_4 , the first member of the series, is greater than those for additional members of the series.

All of the distributions predict that mole fraction (or the ratio m_n/F_n in Eq. (4)) varies logarithmically with carbon number above some minimum C number. Deviations from this relationship, if any, would seem to be most likely for products of low carbon number where the assumption that α is independent of chain length would be expected to be least likely. It is frequently reported that the CH_4 fraction is "higher than expected" and the other low-carbon-number fractions are "lower than expected." Consequently, C_2 groups are sometimes postulated to have a greater reactivity attributed to chain growth on both ends and methane is considered to be formed by additional mechanisms such as cracking. In some cases, especially with cobalt catalysts, these mechanisms may well be true but in many others, especially with iron catalysts, it appears that these conclusions may stem instead from experimental artifacts, from consideration of only certain groups of products rather than the

entire product spectrum, or from use of an inappropriate product distribution prediction (see later). The basic relationship for testing of data is the mole fraction distribution, Eq. (7), which we shall term the Flory distribution.

EXPERIMENTAL

Synthesis gas was passed continuously through a mechanically stirred autoclave about half-filled with an essentially nonvolatile and inert liquid, $n\text{-C}_{28}\text{H}_{58}$, octacosane, in which the finely divided catalyst was suspended. Such a system can be especially effective for fundamental kinetic studies. The entire contents can be well mixed so no gradients of concentration or temperature exist through the reactor. Relatively nonvolatile hydrocarbon products are readily desorbed from the catalyst so accumulation of products in catalyst pores or catalyst fouling is much less likely.

Reactor

The slurry reactor and ancillary equipment are schematically presented in Fig. 1. The stainless-steel, 1-liter autoclave was operated in a semibatch fashion in that syn-

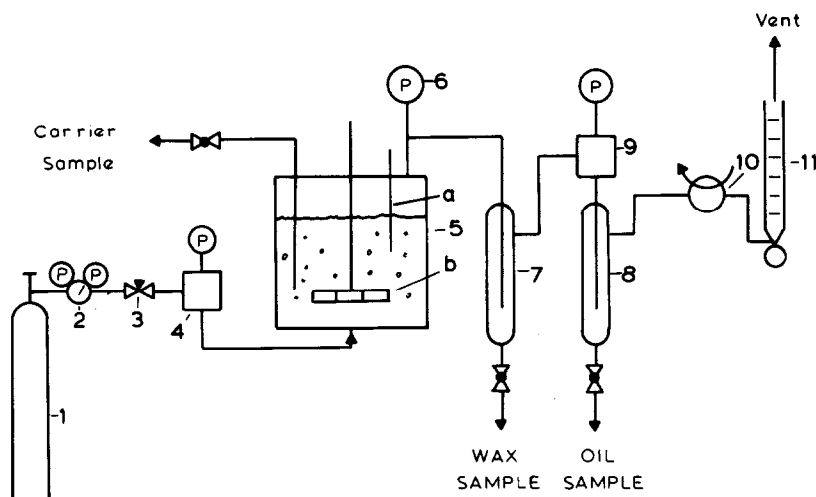


FIG. 1. Slurry reactor apparatus: (1) gas cylinder with premixed CO/H_2 mixture; (2) pressure regulator; (3) automated flow controller; (4) back-pressure regulator; (5) 1-liter, mechanically stirred autoclave with thermocouple at (a) and turbine impeller at (b); (6) pressure gauge; (7) wax receiver; (8) ice-cooled receiver; (9) back-pressure regulator; (10) gas sample valve; (11) soap-film flowmeter.

thesis gas was continually sparged to the slurry in the reactor while volatile products were removed overhead, whereas the catalyst and inert liquid remained in the reactor for the duration of a run (about 20 continuous days on stream). Accumulation of nonvolatile products during this time was small. No heat or mass transfer limitations were present, as evidenced by a negligible change in conversion at faster stirring speeds. This also indicated that the reactor was well mixed. After an initial period, steady-state operation with regard to catalytic activity and carbon number distribution was obtained over the entire run. Experimental parameters studied are summarized in Table 1. Space velocities reported are calculated as inlet gas volumetric flow rate at STP divided by the volume of the liquid carrier present (about $\frac{1}{2}$ liter).

Catalyst

The catalyst (from United Catalysts, Inc. and designated C-73) was a fused iron normally employed for ammonia synthesis. On an unreduced basis, it contained 2.0–3.0% Al_2O_3 , 0.5–0.8% K_2O , 0.7–1.2% CaO , and <0.4% SiO_2 . It was crushed to particle sizes between 170 and 270 mesh and prereduced in a separate vessel with hydrogen at 400°C, atmospheric pressure, and space velocity of 5000 hr^{-1} . It was then slurried with the liquid (*n*-octacosane of >99% purity) to produce a 15-wt% suspension, based on unreduced weight.

TABLE 1

Range of Experimental Conditions

Temperature	234–269°C
Pressure	790 kPa
Space velocity	56–424 v/v/hr (at STP)
Inlet H_2/CO	0.67–1.3
Outlet H_2/CO	0.85–16
Outlet $\text{H}_2\text{O}/\text{CO}_2$	0.022–0.26
H_2 conversion	30–63%
CO conversion	59–96%

Product Analysis

Liquid hydrocarbons and water were condensed in two traps, one operated at about 70°C, and the second at 2°C. In each trap the liquid separated into an oil phase which contained the bulk of the hydrocarbon product and an aqueous phase consisting of water plus oxygenates. These fractions were analyzed by gas chromatography. The material in the 70°C trap contained a small amount of *n*- $\text{C}_{28}\text{H}_{58}$ (bp at atmospheric pressure = 429°C) volatilized from the reactor. Individual species were first identified by spiking experiments with known compounds and peak assignments were checked by gas chromatography/mass spectrometry. Details of these procedures will be published elsewhere. Noncondensable gas samples (containing H_2 , CO , CO_2 , and the various C_1 to C_4 hydrocarbons) were continuously taken with an on-line valve and analyzed by gas chromatography. By the use of a pure liquid in the reactor the slow accumulation of high-molecular-weight products could be clearly distinguished from the starting liquid. The material out of the reactor routinely amounted to 97 to 99 wt% of that charged, based on total mass and individual number of moles of hydrogen, oxygen, and carbon species recovered in the traps and as exit gas. Analysis of the liquid in the reactor at the end of a run indicated that an additional 1 to 2% of the products had accumulated in the reactor.

Although a large number of compounds was produced by the synthesis, they are characterized here only by C number. For

TABLE 2

Range of Product Ratios at 269°C and 790 kPa

Carbon number	α - and β -olefins/ <i>n</i> -paraffins	Oxygenates/total organic
2	2.2–4.3	0.26–0.37
3	6.1–8.2	0.16–0.20
10	3.4–5.1	0.05–0.12

the total of the C_1 to C_{10} fraction, the total product composition amounted typically to about 45 mole% of α - (predominantly) and β -olefins, 35 mole% normal paraffins, and 15 mole% oxygenated hydrocarbons of which normal alcohols and aldehydes together predominated. The remaining 5 mole% included branched olefins and paraffins and a small amount of cyclic compounds. Table 2 gives additional information.

RESULTS

We will show that our products follow the Flory distribution to a remarkable degree, noting especially that C_1 (mostly CH_4) and C_2 fit the same distribution. For this to be true, the primary growth must involve only one unit at a time containing only one carbon atom, and all secondary reactions must result in no change in carbon number. To be sure, secondary effects can lead to products that appear to follow a Flory type of distribution above some minimum carbon number, but then the amount of CH_4 formed would not usually fit the distribution (9).

It is generally believed that α -olefins are primary products and that paraffins are formed from them. Henrici-Olivé and Olivé (5), following Pichler *et al.* (10), argue that alcohols are also formed as primary products. Internal olefin isomerization or formation of branched hydrocarbons by isomerization as secondary reactions would not affect the Flory distribution provided that interconversion between carbon numbers is unimportant. Branching effects, whether as a primary or secondary reaction, were neglected here as the term to account for methyl-substituted isomers f in the model by Anderson *et al.* (3) was about 0.014 for our data which corresponds to an F_n value of only 1.10 for C_{10} hydrocarbons, compared to 1.0 if no branching occurs.

The Flory distribution (Eq. (7)) is more conveniently expressed in a logarithmic form:

$$\ln(m_n) = n \ln(\alpha) + \ln\left(\frac{1-\alpha}{\alpha}\right) \quad (9)$$

A linear plot of $\ln(m_n)$ versus n yields the value of α from either the slope (as $\ln(\alpha)$) or the ordinate intercept (as $\ln(1-\alpha)$ at $n=1$). Agreement between the values of α from the slope and intercept is a check on internal consistency and implies that the Flory distribution is followed. Figure 2 shows six sets of data obtained at 269°C with inlet H_2/CO ratios of 0.67 or 1.3 and various contact times. The percentage conversion of CO varied from 59 to 96, the exit H_2/CO ratio from 0.85 to 13.9. The mole fraction is the sum of all organic species found for each carbon number (alkanes, alkenes, alcohols, etc.). In the light gas range all the points cannot be shown because they overlap one another. The CH_4 make, relative to the total organic product, was essentially the same in all cases.

Note that C_1 and C_2 products fall on the same line as higher C numbers. In spite of the wide range of conditions all the data plotted in this fashion exhibit remarkable consistency. Agreement between the line in the figure, calculated using an $\alpha = 0.67$, and the experimental points is good with a trend away from the correlation for C numbers above about 20. There is no trend with conversion or with the very wide range of H_2/CO ratios present in different runs. A one-parameter equation well describes the carbon number distribution.

The greater scatter in the data at higher carbon numbers is due to increasing experimental error because of the smaller quantities of material formed, e.g., the mole ratio of C_{20} to C_1 hydrocarbons produced is 0.00045. Over a sampling period, the material collected in the wax trap normally contains less than 5 wt% octacosane, which has been volatilized from the reactor. This material in the wax trap is analyzed by gas chromatography using a capillary column and F.I.D. Because of its low volatility (normal boiling point of 429°C) the octacosane may not be completely volatilized in

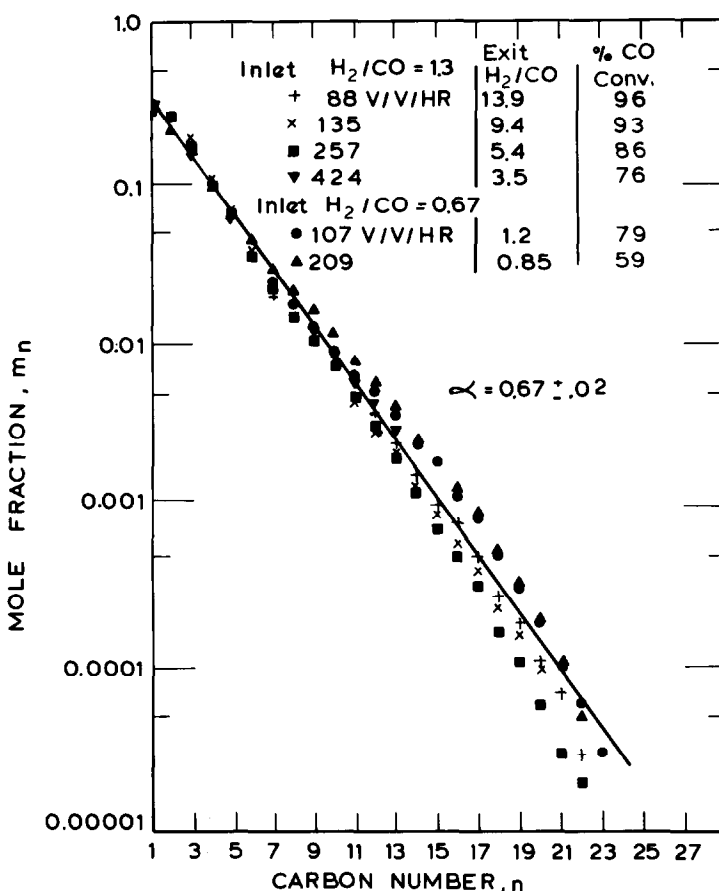


FIG. 2. Application of Flory distribution, 269°C.

the injection port and molecular-weight bias may occur in the capillary splitter. Consequently the amount of octacosane present in the wax trap tended to be slightly underestimated and the reported amounts of individual compounds at carbon numbers greater than about 13 tended to be slightly high. This usually was not very significant but the results became increasingly unreliable when octacosane in the wax trap exceeded about 10%. The amount of octacosane volatilized and collected increases with reactor temperature and higher space velocities, but major difficulties with wax trap analysis occurred here only under the most extreme condition studied (269°C and 424 v/v/hr). Hence on

Fig. 2 no data points are shown beyond C₁₃ for this particular run.

The products of high carbon number ($n > 20$) deviate below the theoretical line because of their increasingly lower volatility. The amount of material m_n depicted in Fig. 2 is determined by those products which volatilize out of the reactor and subsequently are analyzed downstream as either condensed hydrocarbons in the traps or light gas. It is not surprising that some high-molecular-weight material accumulates in the reactor as, for example, the boiling point of n -C₂₀H₄₂ is 343°C at atmospheric pressure. Gas chromatographic analysis of the slurry liquid at the end of the run confirmed the presence of these species.

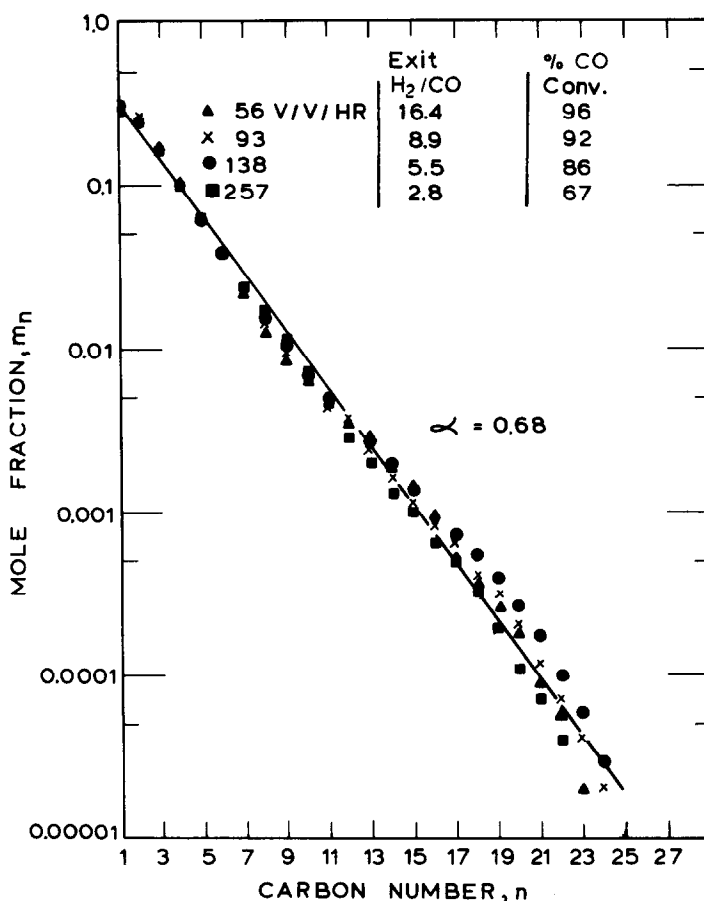


FIG. 3. Application of Flory distribution, 249°C. Inlet H₂/CO ratio = 1.3.

The slight S shape of some of the data points in Fig. 2 about the theoretical linear fit is attributed to experimental artifacts. In order to construct the carbon number distribution, five fractions must be spliced together, i.e., the aqueous and oil phases from each of the two traps together with the noncondensable gases analyzed on stream. The material collected from the trap at 2°C is perhaps the least accurate because of added dead volume in tubing and the back-pressure regulator. The slightly lower-than-expected amount of C₈ to C₁₂ hydrocarbons corresponds to that range of organics collected in this second trap. Better fit could be obtained by slightly adjusting upward

the total weight of products collected in this condenser.

It is remarkable that, within experimental error, the products follow the Flory distribution over more than four orders of magnitude of mole fraction and C numbers from 1 to 20 or more. The agreement of the C₁, C₂, and C₃ fractions with the rest of the distribution is noteworthy. Similar data taken at 249 and 234°C, plotted in the form of Eq. (9), are represented in Figs. 3 and 4, respectively. Once again, up to C₁₇ or C₁₈, the fit of the Flory distribution is good with values of α of 0.68 and 0.71, respectively. Values of α are seen again to be independent of conversion and H₂/CO ratio, and increase

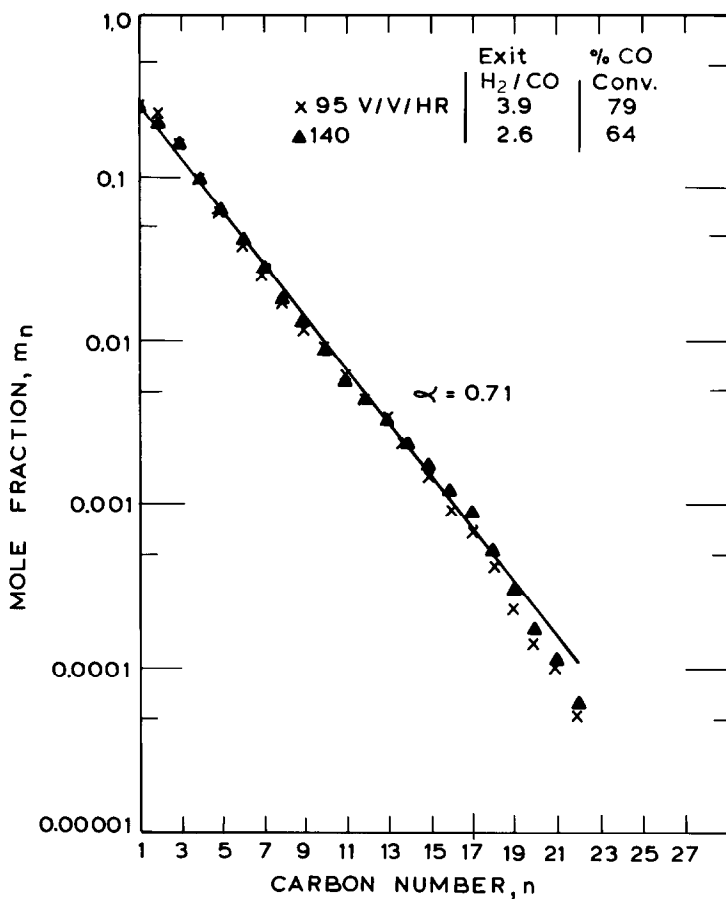


FIG. 4. Application of Flory distribution, 234°C. Inlet H₂/CO ratio = 1.3.

only slightly with decreased temperature over a range of 269 to 234°C.

A previous study provides enough detailed information on product distribution over the entire C number range to allow reanalysis by the Flory distribution. The data of Rheinpreussen A.G., reported by Weingaertner (11) as part of the Schwarzheide tests, are illustrated in Fig. 5. A fixed-bed reactor was employed with an iron catalyst containing 0.5–1.0 parts K₂CO₃, 5 parts copper, and 100 parts Fe on a dolomite carrier, as reported by Anderson (12). We deduce from Anderson that the reaction conditions were 224°C and 1.0 MPa. Agreement between the line in the figure, calculated using $\alpha = 0.70$, and experimental points is good. As in our experi-

mental data, oxygenated compounds are included here with hydrocarbons. Anderson (12) estimated a chain growth probability of 0.67 for these same data by employing Eq. (3), noting that $\alpha = 1/(1 + \beta)$. He calculated this on a nonoxygenate basis and reported the linear portion to be between C₃ and C₉. As discussed later, the slight discrepancy might be caused by neglecting low-molecular-weight alcohols.

DISCUSSION

The number-average molecular weight \bar{M}_n of the product is

$$\bar{M}_n = M_0/(1 - \alpha), \quad (10)$$

where M_0 is the mean molecular weight of

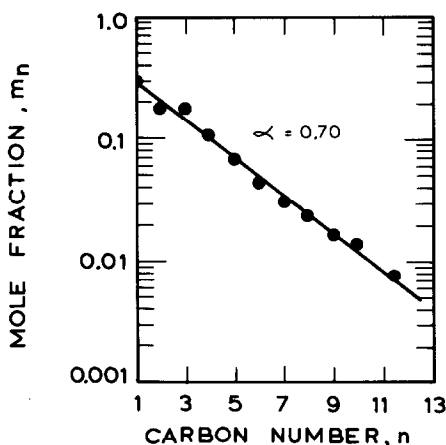


FIG. 5. Application of Flory distribution to industrial Fischer-Tropsch data (after (11)). Iron catalyst in a fixed-bed reactor at 224°C and 1 MPa.

the structural unit. Since α was independent of space velocity in our studies this means that the molecular weight of the product was essentially unchanged by the degree of conversion of carbon monoxide and hydrogen.

Recently Dwyer and Somorjai (13), working with iron single-crystal surfaces, reported that ethylene and propylene, added as such to synthesis gas, markedly shifted the hydrocarbon distribution toward higher hydrocarbons, reporting information for the C_1 to C_5 products. Studies were at 300°C and 610 kPa in a closed system. At a H_2/CO ratio of 3:1, and for total conversions less than 1%, the value of α was 0.30 when 0.04% C_2H_4 was added, 0.56 when 2.7% C_2H_4 was added, and 0.70 when 2.2% C_3H_6 was added.

In an early paper Hall and co-workers (14) showed by tracer studies over iron catalysts that ethylene could be incorporated into growing chains and Schulz *et al.* (15) later showed similar results by use of ^{14}C -labeled olefins, but the effect was much more marked with cobalt than with iron. With an alkalinized iron catalyst at 220°C, 2 MPa, and H_2/CO ratio of 2:1 only 9% of C_2H_4 or 1% of C_3H_7 fed went into the grow-

ing chains. Comparison of the Schulz results with those of Dwyer and Somorjai suggests that possibly the effect is much less pronounced in the presence of alkali.

In any event the molecular weight of the product might be expected to increase with increased contact time which would allow olefins, formed by a primary reaction, a longer opportunity to react. However, a small degree of product reincorporation into growing chains might be difficult to identify as a perturbation from a straight line on a semilogarithmic plot.

In our studies a great deal of intraconversion within each carbon number occurred as contact time was varied (Table 2). Yet the same chain growth probability of 0.67 was obtained even though, for instance, the amount of ethylene present doubled. This implies that although in a plug-flow-type reactor the relative amount of olefins, paraffins, and oxygenates within each carbon number may vary with contact time, the carbon number distribution should not change.

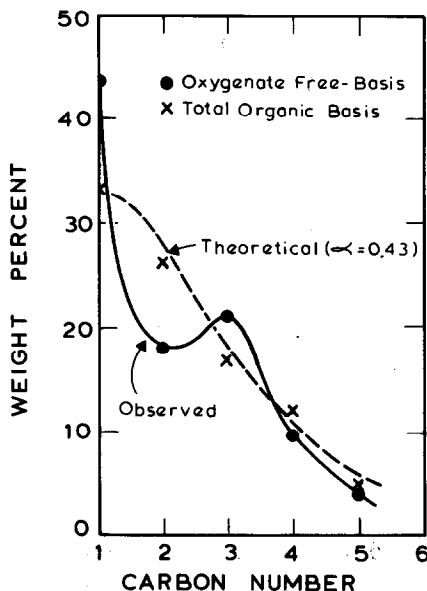


FIG. 6. Carbon number distribution of Fischer-Tropsch products (after (17)) for a nitrided-iron catalyst in a fluid-bed reactor at 252°C and 2.2 MPa.

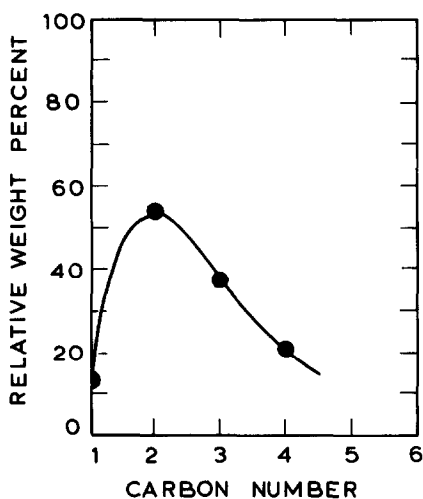


FIG. 7. Percentage oxygenates in each carbon number fraction (after (17)). Nitrided-iron catalyst in a fluid-bed reactor at 252°C and 2.2 MPa.

Our results further imply that there is a common precursor in the formation of Fischer-Tropsch products whose rates of propagation and termination under our conditions have about the same partial pressure and temperature dependency on reaction order. This offers a challenge to mechanistic interpretation. If the precursor is a surface intermediate, this would imply that the rate of termination as CH_4 is the same as the rate of termination as olefin or as an alcohol, which seems unlikely.

Alterations in catalyst composition can alter the average molecular-weight distribution, which corresponds to a change in the value of α . Dry and Oosthuizen (16) demonstrated a correlation between catalyst surface basicity and hydrocarbon selectivity. Alkali promoters of iron, in particular potassium, increase α .

The Schulz or Flory distribution is sometimes applied to Fischer-Tropsch data using a weight fraction comprising the sum of only hydrocarbons at each carbon number, neglecting alcohols and other oxygenated compounds. This can lead to misleading conclusions at lower carbon numbers where significant amounts of oxygenates

are often produced. A study by Demeter and Schlesinger (17), as reported in a review by Baird *et al.* (18), illustrates this point. For a nitrided fused-iron catalyst, operated in a fluidized-bed reactor at 252°C and 2.2 MPa, the results for "period 11" are plotted in Fig. 6 on an oxygenate-free basis. The amount of CH_4 seems to be "too high" and C_2 appears "too low." However, the fraction of alcohols neglected is significant, as portrayed in Fig. 7. Data for all components, plotted in the form of Eq. (9), are represented in Fig. 8, and good agreement with the line in the figure is obtained, calculated using an α of 0.43. The lower value of α is consistent with the reports that nitriding an iron catalyst causes a shift to lighter products, as summarized by Anderson (19). The data of Demeter and Schlesinger are replotted in Fig. 6 on a total organic basis. The theoretical curve, obtained by plotting Eq. (8) for $\alpha = 0.43$, fits the data well.

Some deviations from the Flory distribution may be intrinsic, as might be shown by a catalyst having more than one kind of site, by a catalyst or reacting environment

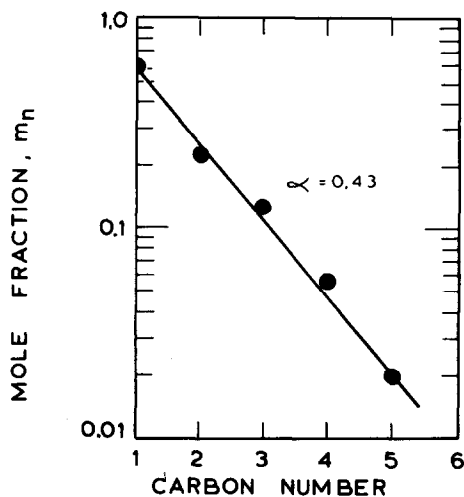


FIG. 8. Application of Flory distribution to pilot plant Fischer-Tropsch data (after (17)) for a nitrided-iron catalyst in a fluid-bed reactor at 252°C and 2.2 MPa.

that produces a different kind of termination process, by reentry of product into growing chains, etc. However, in some cases the entire product distribution was not determined or certain groups of products were not considered. Some investigators report only liquid hydrocarbons and ignore gaseous products, others vice versa. Some report only hydrocarbons and ignore oxygenated products. However, many reported deviations seem to stem from experimental artifacts, which are discussed elsewhere (20).

SUMMARY

Our study of the Fischer-Tropsch synthesis on an alkalized iron catalyst in a well-stirred slurry reactor shows that if products are reported on a total organic basis, the Flory distribution, including CH_4 and other low-carbon-number products, is obtained over a wide range of operating conditions. This probability of chain growth relative to chain termination, given by α , was constant with H_2/CO ratios varying from 0.85 to 16, and increased only slightly with decreased temperature over a 35°C range.

ACKNOWLEDGMENT

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