[CONTRIBUTION FROM THE SYNTHETIC FUELS RESEARCH BRANCH, BUREAU OF MINES]

The Distribution of Liquid and Solid Fischer–Tropsch Hydrocarbons by Carbon Number[*]

BY MILTON MANES

RECEIVED NOVEMBER 7, 1951

An equation has been derived for calculating the distribution by carbon number of Fischer–Tropsch hydrocarbons, based on the assumptions that chain growth in the synthesis proceeds by stepwise addition of single carbon atoms, and that the probability of growth, α, of a given hydrocarbon chain is independent of the carbon number above C_5, although it may vary with experimental conditions. The equation relates the distribution of the liquid and solid product to α. Its applicability to relatively crude fractionation data ("gasoline," "Diesel oil" and "wax") from a wide variety of sources indicates that the approximate constancy of α, previously observed for liquid hydrocarbons, extends to waxes, and that α is a convenient parameter for characterizing the product distribution. The eventual termination of chain growth is a necessary consequence of the equation so that selective cracking of waxes need not be postulated.

Mathematical expressions for the carbon-number distribution of Fischer–Tropsch hydrocarbons have been derived by Herington,[1] Friedel and Anderson,[2] and Anderson, Friedel and Storch,[3] based on the hypothesis that chain growth in the synthesis proceeds by stepwise addition of single carbon atoms. Because of the meagerness of precise fractionation data, the comparison of prediction with experiment was limited to three samples. Moreover, the lack of such data for products above C_{20} prevented application of these equations to waxes.

An equation is derived here for testing the hypothesis of constant growth probability of the carbon chain, using relatively crude fractionation data. The satisfactory correlation of these data in terms of a single parameter shows the wide applicability of the hypothesis. Letting α_n be the probability that a carbon chain of n or more carbons will grow by one carbon atom, and assuming that α_n is constant, *i.e.*, $\alpha_n = \alpha$, under conditions of synthesis, Friedel and Anderson[2] showed that

$$\phi_n = \phi_x \alpha^{n-x} \qquad (1)$$

and

$$W_n \cong 14n\ \phi_x \alpha^{n-x} \qquad (2)$$

where ϕ_x and ϕ_n represent the respective numbers of moles of C_n and C_x hydrocarbons in the product, and W_n is the weight in grams of all C_n hydrocarbons. Starting with these equations one writes the weight of the C_{x+} fraction (containing x or more carbon atoms per molecule) as

$$W_{x+} = \sum_{n=x}^{\infty} W_n \qquad (3)$$

or, from equation (2)

$$W_{x+} \cong 14\phi_x \sum_{n=x}^{\infty} n\alpha^{n-x} \qquad (4)$$

The summation is made as

$$\sum_{n=x}^{\infty} n\alpha^{n-x} = \alpha^{1-x}\ \mathrm{d}/\mathrm{d}\alpha\left(\sum_{n=x}^{\infty} \alpha^n\right) \qquad (5)$$

For $\alpha < 1$

$$\sum_{n=x}^{\infty} \alpha^n = \alpha^x/(1-\alpha) \qquad (6)$$

Substitution of equations (6) and (5) into equation (4) yields

$$W_{x+} \cong 14\ \phi_x[x - \alpha(x-1)]/(1-\alpha)^2 \qquad (7)$$

or, for $r > x$

$$W_{r+} \cong 14\phi_x\alpha^{r-x}\ [r - \alpha(r-1)]/(1-\alpha)^2 \qquad (7a)$$

The ratio W_{r+}/W_{x+}, where $r > x$, is

$$W_{r+}/W_{x+} \cong \alpha^{r-x}\ [r - \alpha(r-1)]/[x - \alpha(x-1)] \qquad (8)$$

Equation (8) makes it possible to test the assumption of constant α by the use of data which had not previously been applicable. For example, for $x = 5$ and $r = 21$, equation (8) gives the ratio of the weight of C_{21+} hydrocarbons to the weight of total liquids and solids as a function of α. If α is measured[1,2] by precise fractionation up to C_{20}, then the observed ratio W_{21+}/W_{5+} should be the same as that calculated from equation (8). The validity of this assumption for the undistilled residue is borne out by the data of Herington[1] and of Friedel and Anderson.[2] Their values for α, 0.83 for their own data and 0.77 for Herington's data, when substituted into equation (8) give the following comparison between prediction and experiment:

for W_{21+}/W_{5+} (Friedel and Anderson), calcd. 13.3%, found 13%;

for W_{12+}/W_{5+} (Herington), calcd. 29.5%, found 31.1%.

A more general application of equation (8) is shown in Fig. 1, where calculated values of W_{r+}/W_{5+} are plotted as ordinates against α as abscissa for a number of values of r. For any value of α, the weight fraction of C_{5+} for any range of carbon numbers may be read off the plot as the difference in the ordinates of the proper curves. If the assumption of constant α is correct, every product distribution may be described by just one parameter, α. By the use of a plot of this sort, one may examine product fractionation data in which the total liquid and solid product is divided into as few as three fractions.

Equation (8) may be applied to data on the fractionation of Fischer–Tropsch liquids and solids into "gasoline," Diesel oil" and a "wax" residue. The boiling ranges of these fractions allow reasonably good estimates to be made of the corresponding

---

[*] For material supplementary to this article order Document 3492 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.00 for photocopies (6 × 8 inches) readable without optical aid. Article not copyrighted.

[1] E. F. G. Herington, *Chem. Ind.*, **65**, 347 (1946).

[2] R. A. Friedel and R. B. Anderson, THIS JOURNAL, **72**, 1212, 2307 (1950).

[3] R. B. Anderson, R. A. Friedel and H. H. Storch, *J. Chem. Phys.*, **19**, 313 (1951).

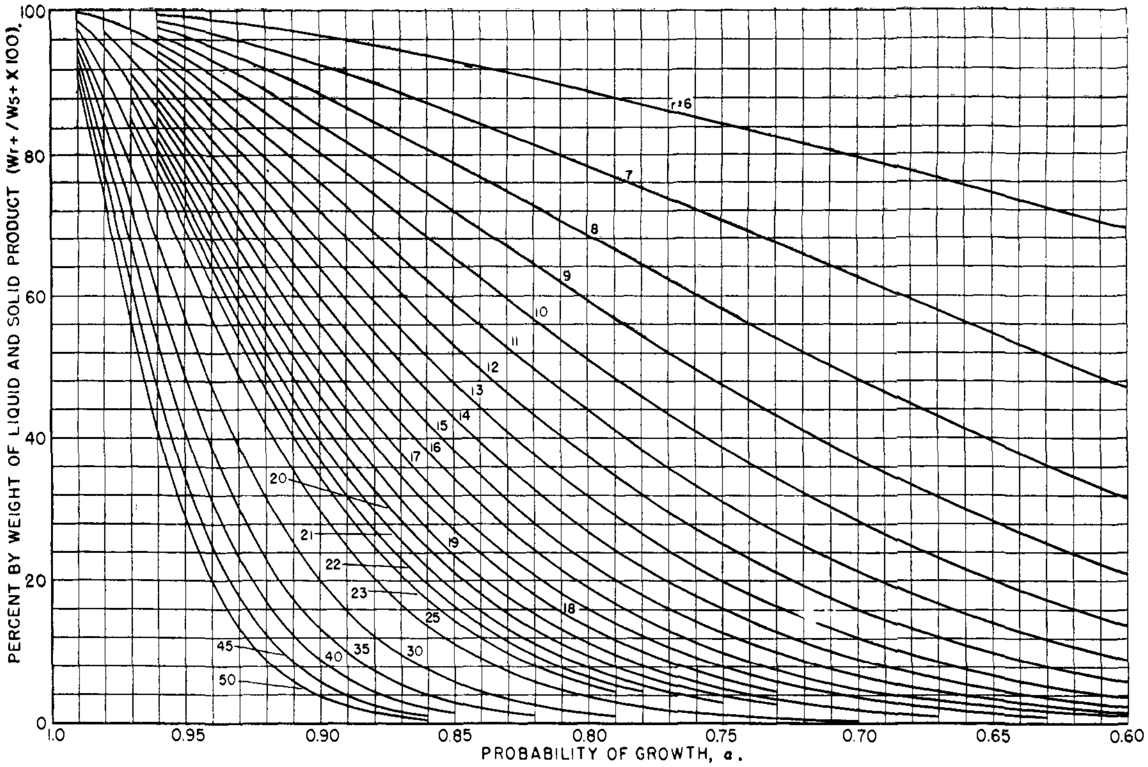

Fig. 1.—Calculated product distributions of liquid and solid Fischer-Tropsch hydrocarbons.

carbon number ranges when the products consist chiefly of hydrocarbons, since the rise in boiling point for each added carbon atom is of the order of 20° and is greater than the difference in boiling points between paraffins and olefins of the same carbon number. For example, if α is constant, the observed product distributions into "gasoline" boiling below 200° (C_5–C_{11}), "Diesel oil" boiling at 200–320° (C_{12}–C_{18}), and a "wax" residue (C_{19+}) should fit the calculated curves for W_{12+}/W_{5+} and W_{19+}/W_{5+}.

The agreement of the calculations with experimental data is illustrated in Figs. 2 to 4. The plotted data were taken from a book by Storch, Golumbic and Anderson.[4] These data, although not exhaustive, come from a large number of independent sources,[5–18] and encompass a wide range of most of the variables encountered in Fischer–Tropsch synthesis. For example, the data deal with products from cobalt catalysts and three types of iron catalysts. Temperatures of operation range from 160 to 330° and pressures from 0.2 to 151 atmospheres. The range of product distributions may be estimated from the graphs. Data in the book were excluded only when the fractionation did not yield the ranges of hydrocarbons indicated on the graphs; when the products (iron catalysts) may have contained large amounts of oxygenated material; and when coincident points were impossible to plot. The calculated curves therefore have been applied to data of very high diversity. The abscissas of pairs of experimental points were chosen to give the best visually-observed fit on both curves. Because the separation temperature was close to the boiling point of one of the hydrocarbons, two lower curves were drawn in Fig. 4.

(4) H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer-Tropsch and Related Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1951.

(5) Ref. 4, p. 195; F.I.A.T. Reel K 21, Frames 906-10, 1,119-21; (Ruhrchemie Tests with Co-Ni catalysts; 10 atm., 190-193°).

(6) Ref. 4, p. 197; F.I.A.T. Reel K 21, Frames 906-10; 1,119-21 (Ruhrchemie Tests with Co-Ni Catalysts; 10 atm., 170-190°).

(7) Ref. 4, p. 198; F.I.A.T. Reel K 21, Frames 1,093-7 (Ruhrchemie Tests with Co-Mn-kieselguhr Catalyst; 10 atm., 160-175°).

(8) Ref. 7 (Ruhrchemie Tests on Wax-Producing Co-ThO_2-kieselguhr and Co-Mn-kieselguhr catalysts; 10 atm.).

(9) Ref. 4, p. 325; F. Fischer, *Brennstoff-Chem.*, 11, 489 (1930); *Ges. Abhandl. Kenntnis Kohle*, 10, 501 (1930). (Co-ThO_2-kieselguhr catalyst, 1-151 atm., 175-200°).

(10) Ref. 4, p. 328; T.O.M. Reel 36, Bag 3,451, Item 13. (Co-ThO_2-MgO-kieselguhr catalyst, 0.2-7.0 atm., 187-196°).

(11) Ref. 4, p. 374-375; T.O.M. Reel 36, Bag 3,451, Item 1. (Ruhrchemie recycle pilot-plant, Co-ThO_2-MgO-kieselguhr catalyst, 7 atm., 204-213°).

(12) Ref. 4, p. 376; T.O.M. Reel 37, Bag 3,450, Item 3 (Ruhrchemie recycle pilot plant; Co-ThO_2-MgO-kieselguhr catalyst, 7 atm., 195-200°).

(13) Ref. 4, p. 379, T.O.M. Reel 36, Bag 3,451, Item 1 (Ruhrchemie Recycle Pilot Plant; Co-ThO_2-MgO-kieselguhr catalyst 7, atm., 190-225°).

(14) Ref. 4, p. 308; H. Pichler, "The Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen," U. S. Bur. Mines Spec. Rept., 1947, 159 pp. Translation reproduced in T.O.M. Reel 259, Frames 467-654; E. H. Reichl, "U. S. Naval Technical Mission in Europe," Rept. 248-55 (1945), 128 pp.; PB 22,841; K. Gordon, *et al.*, Report on the Petroleum and Synthetic Oil Industry of Germany, B.I.O.S. *Overall Rept.*, 1 (1947), pp. 82-103; T.O.M. Reel 134, Section 1B, Item 24. (Results of tests on six diffrent precipitated Fe catalysts; 10 atm., 200-225°).

(15) Ref. 4, p. 415; F.I.A.T. Reel K22, Frames 1,177-84; Reel K-31, Frames 1,108-1,115. (Liquid phase operation using an Fe, Cu, CaO, kieselguhr catalyst, 15 atm., 250-252°).

(16) Ref. 4, p. 400; "The CO + H_2 Synthesis at I.G. Farben," Vol. I, Part C, prepared under the direction of W. Faragher and J. Foucher at Ludwigshafen in 1947. Translation published as F.I.A.T. Final Rept. 1,267, PB 97,368. (Hot-gas-recycle process, Fe catalyst, 20 atm. 320-330°).

(17) Ref. 4, p. 289; R. B. Anderson, unpublished data (Fe synthetic ammonia-type catalyst, 7 atm. 220-266°).

(18) Ref. 4, p. 234; B. Seligman, J. F. Shultz and R. B. Anderson, *Ind. Eng. Chem.*, to be published (Cemented Fe catalyst; 7 atm, 228-280°).

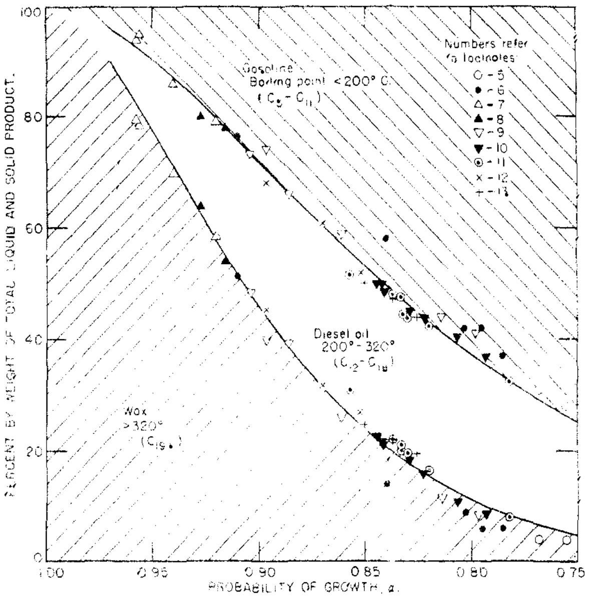

Fig. 2.—Observed product distributions of liquid and solid Fischer–Tropsch hydrocarbons (cobalt catalysts), fitted to Equation (8).

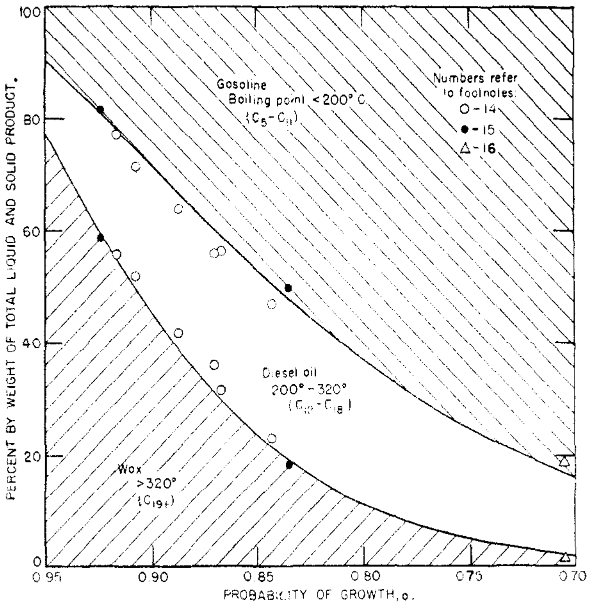

Fig. 3.—Observed product distributions of liquid and solid Fischer–Tropsch hydrocarbons (iron catalysts), fitted to Equation (8).

According to the curves of Figs. 2 and 3, the calculated weight percentage of product boiling between 200 and 320° is at most 29% and decreases gradually over a wide range of larger and smaller values of α. If α is indeed constant, the maximum yield of Diesel oil should be easily approached but never exceeded. As a matter of fact, serious attempts made to increase this yield have been unsuccessful.[19,20] Figure 1 enables one to predict, on the assumption of constant α, the maximum relative yield in any carbon-number range.

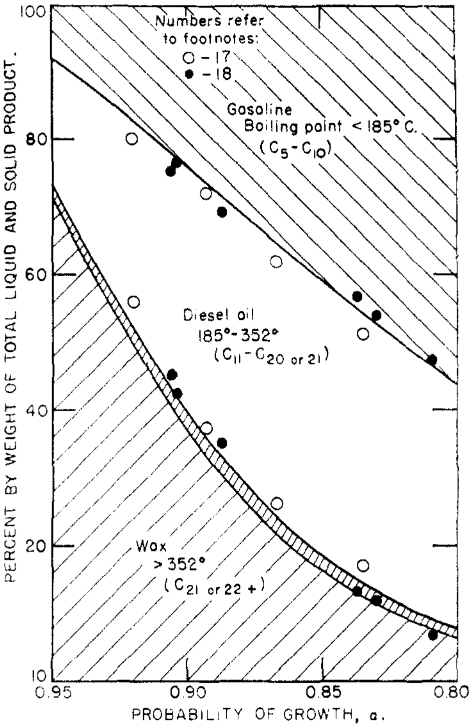

Fig. 4.—Observed product distributions of liquid and solid Fischer–Tropsch hydrocarbons (iron catalysts), fitted to Equation (8).

To a certain extent, the comparative constancy of the relative yield of Diesel oil in synthesis over cobalt and iron increases fortuitously the accuracy of the predicted product distributions. As α may not be constant in time and is not likely to be constant over the length of the catalyst bed, observed product distributions, although fitted to one value of α, probably represent averages of different values of α. In the range of α where the yield of any one fraction (in this case the Diesel oil fraction) is either constant or a linear function of α, variation of α does not affect adversely the correspondence between predictions and data.

According to equation (8), the assumption that α is constant and less than unity suffices to terminate chain growth in effect, since W_{r+}/W_{x+} approaches zero as r approaches infinity. It is therefore not necessary to postulate that chain growth terminates because waxes are particularly susceptible to cracking. Furthermore, the correspondence between calculated and observed distributions gives no evidence for such selective cracking. However, the effect of a possible monotonic change in α becomes harder to detect as the carbon number increases, because the amount of product decreases with increasing carbon number. The results, therefore, do not prove that the assumption of constant α is valid for hydrocarbons of extremely high molecular weights.

The only evidence found thus far which indicates a variation of α with increasing molecular weight is the data of Pichler[4,19] on the fractionation of waxes obtained with ruthenium catalysts. The

---

(19) H. Pichler, U. S. Bur. Mines Spec. Rept., 1947. Translation reproduced in T.O.M. Reel 259, Frames 467–654.

(20) Statement by F. Martin, CIOS File XXVII-70, Item 30, P.B. 415 (1945), p. 64.

TABLE I

COMPARISON OF CALCULATED WITH ACTUAL PRODUCT DISTRIBUTION IN WAX OBTAINED WITH A RUTHENIUM CATALYST

Weight of fraction, g.	Mean molecular weight of fraction	Weight of cumulative fraction, g.	Mean molecular of cumulative fraction	Ave. C no. of cumulative fraction	Carbon number range	Calculated weight per cent.	Actual weight per cent.
16	760	68	1,996	143	40+	100	100
16	1,750	52	3,997	286	183+	50	76
22	6,750	36	9,307	665	562+	3	52
14	23,000	14	23,000	1643	1540+	0.0006	21

pertinent portions of these data are shown in the first two columns of Table I. The weights of the fractions (column 1) were recalculated on a cumulative basis so that they were in the form W_{x+} (column 3). The mean molecular weight of the cumulative fractions was then calculated from the equation

$$M_{ijk}\cdots = \frac{W_i + W_j + W_k + \cdots}{\frac{W_i}{M_i} + \frac{W_j}{M_j} + \frac{W_k}{M_k} + \cdots} \tag{9}$$

where M_{ijk} represents the mean molecular weight of the sum of several fractions, and $W_i \ldots$ (column 1) and $M_i \ldots$ (column 2) are the weights and mean molecular weights of each fraction, respectively. For constant α, the mean molecular weight of each fraction is related to α and to its carbon-number range by the equation

$$M_{x+} = \frac{\sum_x^\infty W_n}{\sum_x^\infty \phi_n} = \frac{14[x - \alpha(x-1)]}{1-\alpha} \tag{10}$$

The substitution, $\bar{C}_x = M_{x+}/14$, where $\bar{C}_{x+}$ is the mean carbon number, gives the equation

$$x = \bar{C}_{x+} - \frac{\alpha}{1-\alpha} \tag{11}$$

Values of $\bar{C}_{x^+}$ are calculated from the experimental data by equation (9) and listed in column 5. Since $\bar{C}_{x^+}$ is related to x and α by equation (11), one may calculate α if the value of x for any cumulative fraction is known. It is assumed here that x for the lightest fraction is 40, *i.e.*, that the product extends from C_{40} to C_∞. The corresponding value of α is then 0.99038. Substitution of this value of α and of the values of $\bar{C}_{x^+}$ (column 5) into equation (8) gives the carbon-number ranges of the cumulative fractions (column 6) and the calculated distribution (column 7). Comparison of columns 7 and 8 shows that the assumption of constant α leads to a predicted value for the weight of the heaviest fraction which is too low by several orders of magnitude. The assumed value of $x = 40$ is as low an estimate as can reasonably be made and hence, by equation (9), if α is constant it cannot be higher than 0.99038. Therefore, the data can be explained only on the assumption that α increases with increasing carbon number in the region of the very heavy waxes which comprise a significant fraction of the total weight only in the case of the ruthenium product.

A possible use of the unifying concept of α is as a parameter to describe the shift in product distribution with changing experimental conditions. For example, the decrease of α with increasing temperature counteracts the increased space–time yield of products and therefore affects determinations of activation energy. This problem will be considered elsewhere.

Acknowledgments.—The author is indebted to Dr. L. J. E. Hofer for discussing this problem and making many helpful suggestions; and to Dr. Hofer, Mr. E. M. Cohn and Dr. R. B. Anderson of the Bureau of Mines, and Dr. P. H. Emmett of Mellon Institute for reviewing and commenting upon the manuscript.

BRUCETON, PENNA.