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The molecular weight distribution of the products of the Fischer–Tropsch synthesis

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Abstract. The literature data on the principal types of experimental molecular-weight distributions in the products of the Fischer–Tropsch synthesis are examined and classified. The influence of the catalyst composition and the experimental conditions in the Fischer–Tropsch synthesis on the type of molecular weight distribution is considered. The possible mechanisms of the propagation and termination of the hydrocarbon chain in the Fischer–Tropsch synthesis are discussed using the available data on the molecular-weight distribution. The bibliography includes 94 references.

I. Introduction

The study of the molecular weight distribution (MWD) in the products obtained in the Fischer–Tropsch (FT) synthesis constitutes a rapidly developing field of research. Data on the MWD of the products obtained are quoted in virtually every study published after 1980 and devoted to the FT synthesis. These data are of great interest in understanding the mechanism of the FT synthesis and can serve as a basis for the regulation of the process selectivity — an important and complex problem. The increase in the number of publications on this aspect of research has been caused to some extent by the advances in the development of methods for the determination of the quantitative and qualitative compositions of multicomponent mixtures of organic compounds — in the first place high prerformance gas–liquid capillary chromatography and chromatograph-linked mass spectrometry.

Insufficient attention has been devoted to the molecular weight distribution in the monographs and reviews on the FT synthesis.[1–9] For example, the eighth chapter of the book 'Chemical Substances from Coal'[1] is wholly devoted to the FT synthesis but there are no MWD data. In the monographs,[10,11] the examination of the MWD is restricted to data obtained up to 1980 inclusive. It has therefore become necessary to survey theoretical and experimental studies on the MWD which have appeared in the literature during the last 15 years.

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II. Models of the molecular weight distribution

The experimental molar distribution of the n-alkanes obtained in the FT synthesis as a function of the number of carbon atoms in the molecule was first formulated by Herington[12] [Table 1, Eqn (1)]. It follows from Eqn (1) that the ratio β_n of the mole fraction m_n of an n-alkane with n carbon atoms in the molecule to the sum of the mole fractions of n-alkanes containing between $n + 1$ and ∞ carbon atoms is constant.

On the basis of experimental MWD data for hydrocarbons produced by the FT synthesis, Anderson et al.[13] obtained Eqn (2), from which it follows that the ratio α of the mole fractions of n-alkanes containing $n + 1$ (m_{n+1}) and n (m_n) carbon atoms in the molecule is independent of n within the limits of experimental error. The parameter α of the distribution of the FT synthesis products is in the range $0 < \alpha < 1$. It is easy to show that, when β_n is independent of n, the parameters α and β are linked by the following relation:

$$\alpha = \frac{1}{1+\beta}.$$

Eqns (1) and (2) were obtained by analysing multicomponent† products which consisted mainly of a mixture of n-alkanes. An attempt has been made[14] to derive an equation for the distribution of the FT synthesis products, incorporating, apart from hydrocarbons, an appreciable amount of oxygen-containing compounds (mainly alcohols). Eqn (3), describing the MWD for alcohols, was obtained by combining the familiar formulae for the m_n term, i. e.

$$m_n = m_1^{n-1},$$

and the sum of n terms, i. e.

$$\sum_{n=1}^{\infty} m_n = \frac{m_1}{1-\alpha},$$

of an infinitely diminishing geometrical progression, where α is the denominator of the progression. Shuikin et al.[14] understood by $\sum m_n$ the sum of the numbers of moles (or quantities proportional to them) of the oxygen-containing compounds formed in the FT synthesis. The experimental data on the composition of the oxygen-containing compounds were treated in terms of Eqn (3′) — the logarithmic form of Eqn (3). The dependence of MWD on n for n-alkanols, expressed by a plot of $\lg m_n$ against n,

† The components of the FT synthesis products are understood as organic compounds of one class (n-alkanes, n-alkanols, etc.).

Table 1. Equations describing the molecular weight distribution for the FT synthesis products.

Equation	Number of equation	Author(s) of equation	FT synthesis products to which the equation was first applied	Ref.
$m_n = \beta_n \sum_{n=1}^{\infty} m_{ni}$	(1)	Herington	n-Alkanes	12
$m_n = m_{ni}\alpha^{n-1}$	(2)	Anderson, Friedel, and Storch	"	13
$m_n = (1-\alpha)\sum_{n=1}^{\infty} m_{ni}\alpha^{n-1}$	(3)	Shuikin, Kryukov, and Bashkirov	n-Alkanols	14
$\lg m_n = \lg\left[(1-\alpha)\sum_{n=1}^{\infty} m_{ni}\right] + (n-1)\lg\alpha$	(3′)	"	"	
$g_n = (\ln^2\alpha)\, n\alpha^n$	(4)	Schulz	n-Alkane, n-alkanols, and n-alkylamines	15, 18
$\lg(g_n/n) = \lg(\ln^2\alpha) + n\lg\alpha$	(4′)	"	"	
$m_n = (1\alpha)\alpha^{n-1}$	(5)	Flory	n-Alkanes, alkenes, and alkanols	19
$\lg m_n = \lg[(1\alpha)/\alpha] + n\lg\alpha$	(5′)	"	"	
$\lg m_n = \lg(1\alpha) + (n-1)\lg\alpha$	(5″)	"	"	
$g_n = (1\alpha)^2 n\alpha^{n-1}$	(5‴)	Madon	n-Alkanes	20

Note. m_n and g_n are respectively the mole and weight fractions of the components of the FT synthesis products with n carbon atoms in the molecule.

has the form of a straight line, which shows that this equation is applicable to the description of the MWD for the oxygen-containing FT synthesis products.

1. The Anderson–Schulz–Flory distribution

Until the publication of the study of Henrici-Olive and Olive,[15] the analysis of the MWD for the FT synthesis products was not systematic. The authors of this and a series of subsequent studies, surveyed in a monograph,[11] applied to the description of the MWD for the FT synthesis products the Schulz[16] [Eqn (4)] and Flory[17] [Eqn (5)] equations familiar in polymer chemistry. These equations were derived for the analysis of the MWD for polymers obtained respectively by radical polymerisation and linear polycondensation. The MWD calculated by Eqns (4) and (5) are similar for $\alpha > 0.5$,[11,15] so that both equations can be applied with equal success. The logarithmic forms of the Schulz equation [Eqn (4′)] and the Flory equation [Eqns (5′) and (5″)] are more convenient for analysis. As an illustration, Fig. 1 presents the theoretical MWD for a monofunctional product calculated by Eqn (5‴) for $\alpha = 0.9$. Here one may note that there exists an internal check of the agreement between the distribution and Eqns (4′) and (5′) or (5″) based on the equality of the values of α calculated by two independent methods—from the slope of the straight line (α_{sl}) and from the intercept on the ordinate axis (α_{int}). The possibility of describing the MWD for the products with the aid of the Schulz and Flory equations confirms the idea that the polycondensation and polymerisation processes and the mechanism of the formation of C–C bonds in the FT synthesis are all related. By analogy with the polycondensation and polymerisation processes, the parameter α for the FT synthesis occurring under stationary conditions can then be defined by the relation

$$\alpha = \frac{r_p}{r_p + r_t},$$

where r_p and r_t are the rates of propagation and termination of the carbon chain respectively. Here it is assumed that α is independent of chain length.

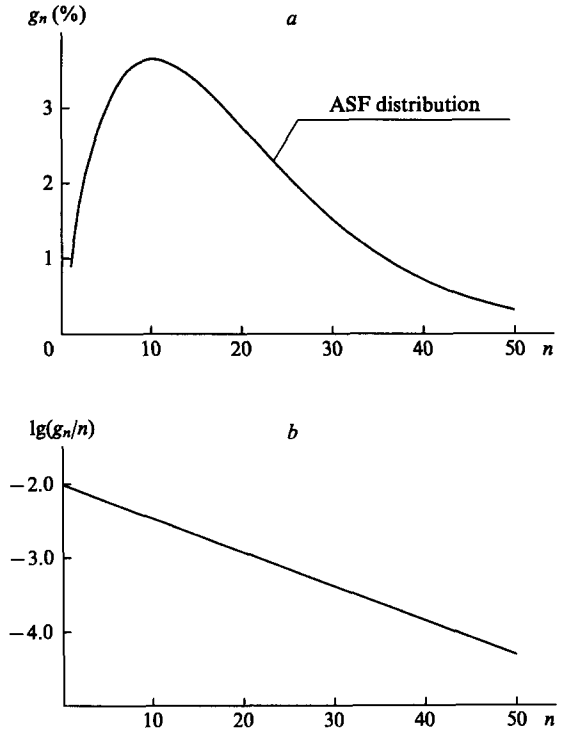


Figure 1. The Anderson–Schulz–Flory normal distribution for the FT synthesis product with $\alpha = 0.9$.[25] (*a*) $g_n - n$ plot; (*b*) semilogarithmic $\lg(g_n/n) - n$ plot.

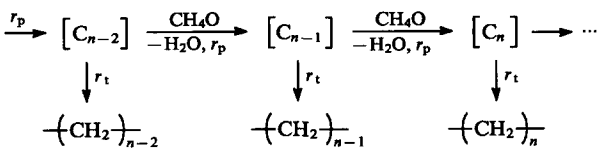
Evidently, the Schulz and Flory equations are applicable to the MWD for the products of the FT synthesis proceeding in accordance with Scheme 1 and the formal Scheme 2 when a polymer having the composition C_nH_{2n} is formed from n hypothetical monomers having the empirical formula CH_4O. Strictly speaking, only alkenes correspond to the polymer in the product.

Scheme 1

$$n(CO+2H_2) \longrightarrow \text{-}(CH_2)_n\text{-} + nH_2O$$

monomer polymer

Scheme 2



Here C_{n-2}, C_{n-1}, and C_n are intermediates with $n-2$, $n-1$, and n carbon atoms respectively.

In the general case, a multicomponent product is formed in the FT synthesis. It consists mainly of alkanes, alkenes, alkanols, and alkanals with a normal structure and contains from 1 to 100 or more carbon atoms.[21,22] The attempts to apply Eqns (4′) and (5′) or (5″) to the description of the MWD for the real products were unsuccessful because of the failure of the internal check of the MWD in terms of α. This difficulty can be partially obviated by applying Eqns (4′) and (5′) or (5″) separately to each component of the FT synthesis product (alkanes, alkanols, etc.). It is noteworthy that Eqn (3′) is transformed into Eqn (5″) if the sum of the moles of the components is unity:

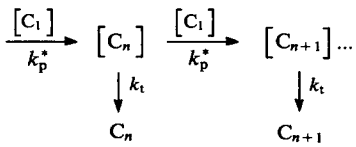
$$\sum_{n=1}^{\infty} m_n = 1.$$

Following Henrici-Olive and Olive,[15] other investigators also began to refer to the molecular weight distributions obeying Eqns (4′) and (5″) as the Schulz–Flory (SF) distributions. At the present time the term Anderson–Schulz–Flory (ASF) distribution is more often employed in the literature.

2. Special problems of the Anderson–Schulz–Flory distribution

A number of problems arise when the ASF distribution is applied to the analysis of real multicomponent FT synthesis products obtained under stationary and nonstationary conditions complicated by the occurrence of secondary reactions, various types of termination of the hydrocarbon chain, and other factors. Before proceeding to their discussion, it is appropriate to return yet again to the consideration of the classical model on the basis of which Eqns (4) and (5) may be obtained. Consider Scheme 3.

Scheme 3

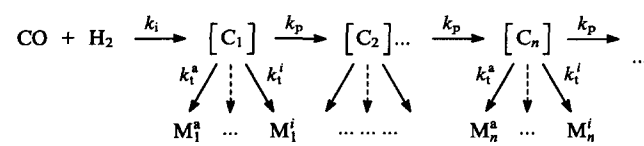


Here $[C_1]$, $[C_n]$, and $[C_{n+1}]$ are the concentrations of intermediates with 1, n, and $n+1$ carbon atoms on the surface of the catalyst, and k_p^* and k_t are the hydrocarbon chain propagation and termination constants respectively.

By use of Scheme 3, the above equations can be derived on the basis of the following postulates: the propagation of the carbon chain takes place as a result of the addition of the C_1 intermediate; chain termination is the result of simple desorption; k_p^* and k_t are independent of the length of the carbon chain. It is then evident that for stationary FT synthesis we have $[\dot{C}_n] = 0$ and, when $k_p = k_p^*[C_1]$ and $\alpha = k_p/(k_p = k_t)$, it is easy to obtain, for example, Eqn (5). In this case, the state involving the formation of the $[C_1]$- intermediate from CO and H_2 (the initiation stage) is unimportant for the derivation of the equation.

Multicomponent products of the FT synthesis. The attempts to apply Eqns (4) and (5) to the analysis of the MWD for real multicomponent FT products, which were unsuccessful because of the failure of the internal check of the MWD in terms of α, were already mentioned above. Eqn (5″) has been derived[23] for the multicomponent FT synthesis products on the basis of the following model (Scheme 4):

Scheme 4



Here $[C_1]$, $[C_2]$, and $[C_n]$ are the concentrations of the intermediates with 1, 2, and n carbon atoms on the catalyst surface, k_i and k_p are the initiation and carbon chain propagation rate constants, k_t^a and k_t^i are the carbon chain termination rate constants for the formation of an alkanol and the ith component of the FT synthesis product, and M_1^a, M_n^a, M_1^i, and M_n^i are the alkanols and the ith components of the product with 1, ..., n carbon atoms respectively.

The derivation of the MWD equation for a multicomponent FT synthesis product involves an increase in the number of postulates from three to five. A further two postulates are added to those described above for the classical model of the ASF distribution: the product components with the same number of carbon atoms n are formed from the C_n intermediate via parallel pathways; the constants for the termination of the carbon chain of the alkanol and the ith components are independent of chain length.

In the stationary state, the rate of initiation r_i is equal to the sum of the rates of termination, i. e.

$$r_i = \sum^{i} r_t^i = \sum^{i} k_t^i \sum_{n=1}^{\infty}[C_n], \tag{6}$$

$$[\dot{C}_1] = \sum^{i} k_t^i \left(\sum_{n=1}^{\infty}[C_n] - k_p[C_1] - \sum^{i} k_t^i[C_1] \right) = 0,$$

$$[\dot{C}_2] = k_p[C_1] - k_p[C_2] - \sum^{i} k_t^i[C_2] = 0, \tag{7}$$

.....

$$[\dot{C}_n] = k_p[C_{n-1}] - k_p[C_n] - \sum^{i} k_t^i[C_n] = 0.$$

Simultaneous solution of Eqn (6) and Eqns (7), taking into account

$$k_p \Big/ \left(k_p + \sum^{i} k_t^i \right) = \alpha,$$

makes it possible to obtain the Flory equation for the intermediates:

$$[C_n] \Big/ \sum_{n=1}^{\infty}[C_n] = (1-\alpha)\alpha^{n-1}. \tag{8}$$

It is seen that $[C_n]/[C_{n-1}] = \alpha$ and, since $[M_n^i] = k_t^i[C_n]$ and $[M_{n-1}^i] = k_t^i[C_{n-1}]$, we have

$$\frac{[M_n]}{[M_{n-1}]} = \alpha . \tag{9}$$

It follows from Eqn (9) that, when the propagation of the carbon chains of the components of the FT synthesis products takes place in accordance with Scheme 4, then the data for the composition of such products, expressed in terms of the semilogarithmic variables of the Flory equation, should fit on straight lines with the same slope. Having solved the equations

$$\begin{aligned} \sum^i [\dot{M}_1^i] &= \sum^i k_t^i[C_1] , \\ \sum^i [\dot{M}_2^i] &= \sum^i k_t^i[C_2] , \\ &\cdots\cdots\cdots\cdots \\ \sum^i [\dot{M}_n^i] &= \sum^i k_t^i[C_n] , \end{aligned} \tag{10}$$

we obtain, after integrating the expression for the mole fraction of the ith components of the products,

$$\sum^i m_n^i = \sum^i [M_n^i] \Big/ \sum_{n=1}^{\infty} \left(\sum^i [M_n^i] \right) = (1-\alpha)\alpha^{n-1} , \tag{11}$$

$$\sum^i g_n^i = n(\ln^2 \alpha)\alpha^n . \tag{11'}$$

Eqns (11) and (11') represent the Flory [Eqn (5)] and Schulz [Eqn (4)] equations for a multicomponent product. The differences between Eqns (11) and (5) and between Eqn (11') and Eqn (4) consists in the fact that the left-hand side of Eqn (11) contains the sum of the mole fractions, while in Eqn (11') it contains the sum of the mass fractions of the ith components of the product with the same number of carbon atoms. An equation analogous to Eqn (11) for the special case of the formation of n-alkanes and n-alkanols has also been obtained by O'Young and Buchwalter.[24]

Chain propagation with two intermediates. In contrast to the classical model of the ASF distribution, the propagation of the carbon chain of a multicomponent product with participation of two intermediates, C_1 and C_2, has been examined.[25] In this case, the rate of formation of the C_n intermediate in the stationary state with $n \geqslant 3$ is described by the equation

$$[\dot{C}_n] = k_p[C_{n-1}] - k_p[C_n] - k_t[C_n] + k_p^*[C_{n-2}] - k_p^*[C_n] = 0 \tag{12}$$

Here the MWD parameter α^* is defined by the relation

$$\alpha^* = \frac{k_p}{k_p + k_t + k_p^*} = \frac{\alpha}{1 + y\alpha} , \tag{13}$$

where $y = k_p^*/k_p$.

An analytical solution of Eqn (12) has been described.[25] Fig. 2 presents the calculated MWD curves for two values of y. Evidently, the curves have an oscillatory form.

The dual nature of chain termination. A more involved version of the termination of the carbon chain, determined by the possibility that part of the monocomponent product with n carbon atoms is formed as a result of the interaction of the intermediates with $n - m$ and m carbon atoms in the molecule,

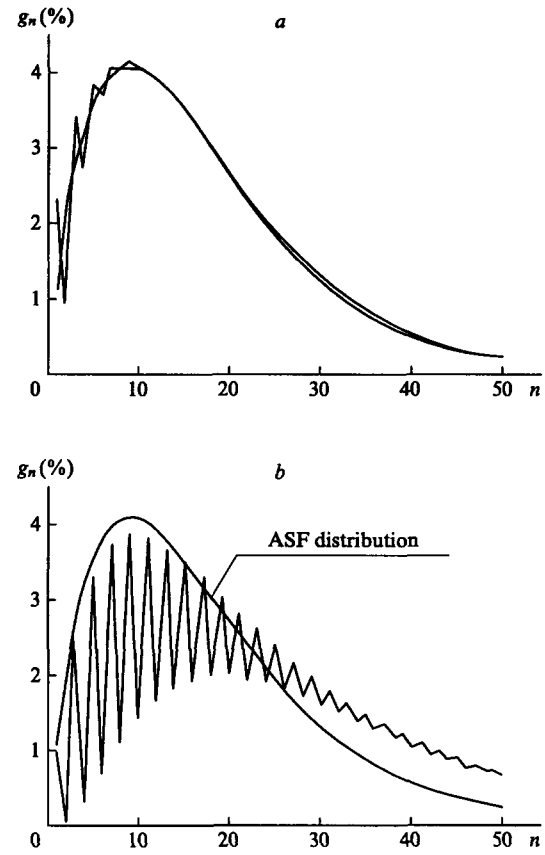


Figure 2. Molecular weight distribution for the FT synthesis products in the case where the carbon chain is propagated with participation of C_1 and C_2 intermediates for different values of y: (*a*) 1; (*b*) 10.[25]

has been analysed.[25] In this case, the rate of formation of the C_n intermediate in the stationary state is described by Eqn (14), such termination being taken into account by the term $k_t'[C_n]$:

$$[\dot{C}_n] = k_p[C_{n-1}] - (k_p + k_t + k_t')[C_n] = 0 . \tag{14}$$

The MWD parameter α' for this case is defined by the relation

$$\alpha' = \frac{k_p}{k_p + k_t + k_t'} = \frac{\alpha}{1 + \mu(1-\alpha)} , \tag{15}$$

where $\mu = k_t'/k_t$.

The exact solution of Eqn (14) has been published.[25] Fig. 3 presents as an illustration the calculated MWD curve for $\mu = 2.7$. It is seen that the selectivity with respect to C_{10} under the conditions of the dual type of termination of the carbon chain is higher than the selectivity for the ASF distribution.

MWD taking into account the propagation of the carbon chain with participation of the products formed as well as the possibility of the cracking of these products have also been examined.[25,26] However, such MWD are so far of purely theoretical importance because under real conditions the contribution by such reactions of the FT synthesis products is extremely low.[27]

Molecular weight distribution for branched FT synthesis products. Depending on the conditions of the FT synthesis, its products may contain different (sometimes appreciable—up to 10%) amounts of alkanes with a branched carbon skeleton—mainly 2- and 3-monomethyl-substituted isomers. The MWD for such hydrocarbons were first examined by Anderson and

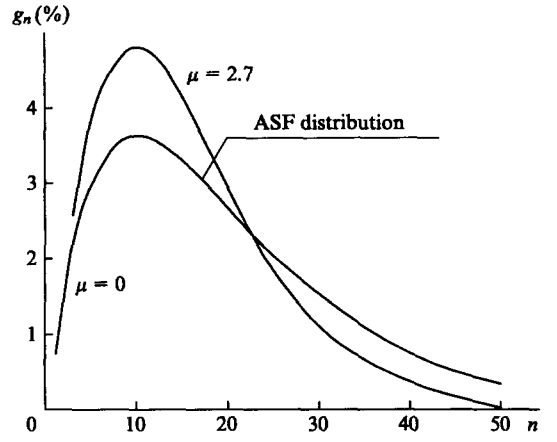
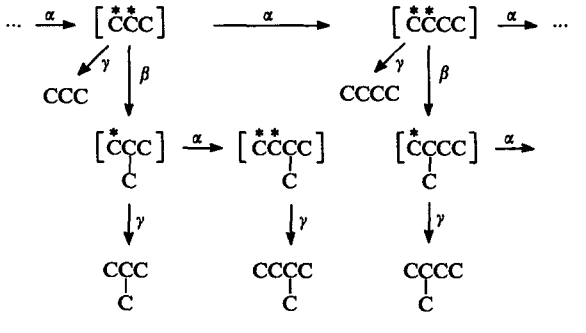


Figure 3. Molecular weight distribution for the FT synthesis product under the conditions of mutual termination of the carbon chain.[25]

coworkers.[28–31] There exist several models of the propagation of the carbon chain of isoalkanes differing from one another by the number of limitations and the extent to which the isomeric composition of the alkanes is taken into account.[10,28–35] In the most complete form, these models have been described by Wojciechowski.[35] We shall confine ourselves to the consideration of Anderson's model.[10]

Evidently the problem associated with the estimation of the proportions of isoalkanes arises in the case of a carbon chain containing four carbon atoms in the molecule. It is then postulated that there is no isomerisation of the normal carbon chain. In this connection, we shall consider a fragment of the model of the propagation of an isomeric alkyl chain (Scheme 5).

Scheme 5



Here $[\overset{**}{C}CC]$, $[\overset{**}{C}CCC]$, $[\overset{*}{C}(C)C]$, $[\overset{*}{C}(C)CC]$ are the concentrations of the intermediates with the normal and isomeric carbon chains on the surface of the catalyst; the asterisks denote the carbon atoms to which the addition of the intermediate $[C_1]$ is postulated, α and β are the propagation rate constants for the normal and isomeric carbon iso-chains respectively, and γ is the rate constant for the termination of the carbon chain in the n-alkanes and isoalkanes.

In the stationary state two equations can be written for the intermediate containing four carbon atoms: for the isomers with the normal $[C_4]$ and branched [*iso*-C_4] chains:

$$\dot{[C_4]} = \alpha[C_3] - \alpha[C_4] - \gamma[C_4] - \beta[C_4] = 0, \quad (16)$$

$$\dot{[iso\text{-}C_4]} = \beta[C_3] - \gamma[iso\text{-}C_4] - \alpha[iso\text{-}C_4] = 0. \quad (17)$$

The following relations can be obtained readily from Eqns (16) and (17):

$$\frac{[C_4]}{[C_3]} = \frac{\alpha}{\alpha + \gamma + \beta} = a,$$

$$\frac{[iso\text{-}C_4]}{[C_3]} = \frac{\beta}{\alpha + \gamma} = b.$$

If the notation $b/a = f$ is used, then the concentration of isobutane relative to that of n-butane depends only on f.

Anderson[10] obtained the following MWD equation for isomeric alkanes — the products of FT synthesis:

$$g_n = \frac{g_3 n F_{(n)} a^{n-3}}{3} \quad \text{for } n \geqslant 4, \quad (18)$$

where

$$F_{(n)} = 1 + (n-3)f + \frac{(n-4)(n-5)f^2}{2} + \ldots .$$

Data on the compositions of the isomeric and normal alkanes are usually expressed in a tabular form.

The special problems of the ASF distribution are not exhausted by the examples examined. Thus the kinetic parameters of the FT synthesis have been determined from MWD data.[35,36] A method has been proposed for the calculation of α as a function of the ratio H_2/CO.[37,38] Using the method of chemical potentials, an equation has been derived for the description of the ASF distribution.[39]

III. Experimental molecular weight distributions

Very many publications have been devoted to the experimental study of the MWD for monocomponent and multicomponent FT synthesis products. In most cases, the experimental MWD obey satisfactorily the ASF distribution (Fig. 1*b*), i.e. are assumed to be normal MWD.[11,15,19,40–47] At the same time, there is a large number of MWD characterised by deviations from the normal ASF distribution. In terms of the semilogarithmic variables of the Schulz and Flory equations, these deviations are manifested either by the curvature of the MWD or are associated with the appearance of different kinds of breaks on the linear MWD plots. However, in such cases the possibility, in principle, of describing part of the experimental MWD by the Flory and Schulz equations remains.

We shall examine the types of experimental MWD most frequently encountered (Fig. 4).

1. The molecular weight distribution characteristic of hydrocarbon FT synthesis products with an enhanced content of methane.[11,15,48,49] The composition of the hydrocarbons, with the exception of the C_1 product, corresponds to the ASF distribution. The maximum of the distribution, corresponding to the C_1 product is probably associated with the existence of an additional path to its formation, either via the $[C_1^*]$ intermediate, different from the $[C_1]$ intermediate, with the participation of which other hydrocarbons are obtained, or via the $[C_1]$ intermediate, which is converted into the C_1 product on other active centres of the catalyst, or, finally, via the intermediate $[C_1^*]$, which is in addition transformed on other active centres of the catalyst.

2. The molecular weight distribution characteristic of hydrocarbon FT synthesis products with a reduced content of C_2 products.[11,15,50–56] The reduced content of ethane and ethylene compared with the normal ASF distribution can be due to several causes in such cases: the propagation and termination of the carbon chain with participation not only of the $[C_1]$ intermediate but also the $[C_2]$ intermediate and secondary reactions involving C_2 products, for example the hydroformylation of ethylene.[57] Sometimes the breaks on the

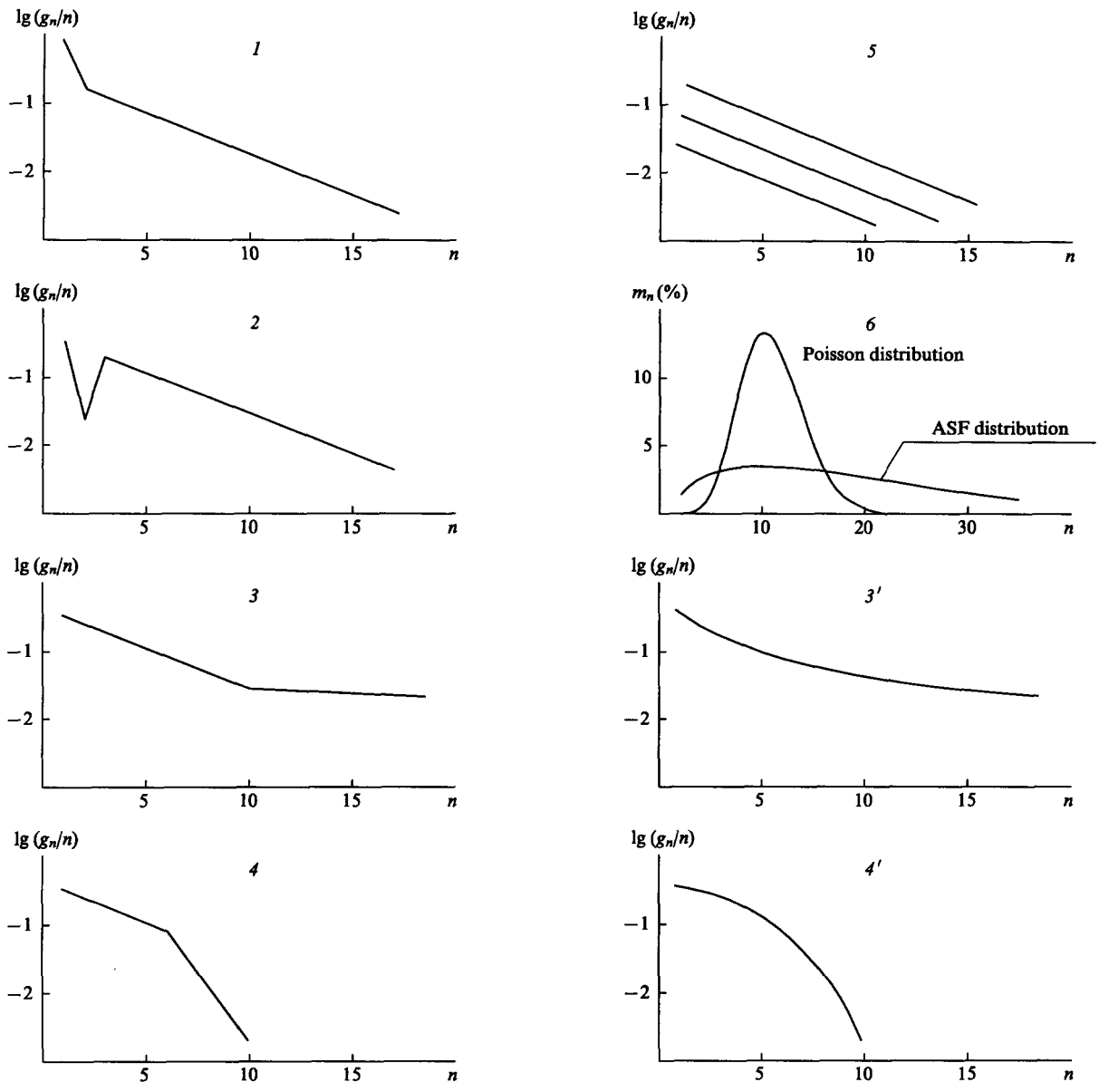
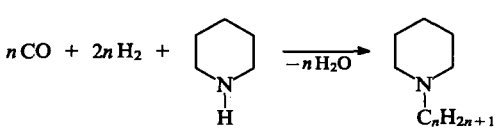


Figure 4. Different types of experimental MWD for the FT synthesis products: (*1*)–(*6*) see text.

linear distribution plots correspond to the C_3-C_4 products[11] which is probably due to the same causes as for the C_2 products. More complex cases, representing a combination of versions *1* and *2*, are encountered.[11,58,59]

3. The molecular weight distribution characteristic of the case where α increases with increase in n. This type of MWD is encountered for alkanes,[34,53,58–73] alkanols,[74] and alkylamines.[75,76] The last can be obtained, for example, in the piperidine-modified FT synthesis in accordance with Scheme 6.

Scheme 6



The break on the MWD curves for alkanes, alkanols, and alkylamines is usually observed at $n = 5-13$, the parameter α for low-molecular-weight products (α_1) being smaller than for high-molecular-weight products (α_2). If the degree of nonlinearity of the MWD is determined in terms of $\Delta\alpha = \alpha_2 - \alpha_1$, then it amounts to 0.12–0.20 for alkanes,[60,66] 0.26 for alkanols,[74] and 0.20 for alkylamines.[75,76] In some cases, there is no break on the MWD curves. Such MWD constitutes type *3'*. The appearance of MWD of types *3* and *3'* can arise from the following causes: the nonstationary nature of the FT synthesis, as a result of which α increases significantly during the period necessary for the collection of the FT synthesis products for analysis; the presence on the catalyst surface of two or more types of active centres on which products with different values of α are obtained;[7,60] the increase in the probability of the propagation of the carbon chain, which is proportional to the number of carbon atoms in the molecule. Several equations have been proposed for the description of MWD of types *3* and *3'*.[60,76,77] The simplest of these is based on the Flory equation [Eqn (5)] and has the following form:

$$m_n = x(1-\alpha_1)\alpha_1^{n-1} + (1-x)(1-\alpha_2)\alpha_2^{n-1}, \qquad (19)$$

where x and $1-x$ are the fractions of the products having the molecular weight distribution parameters α_1 and α_2 respectively.

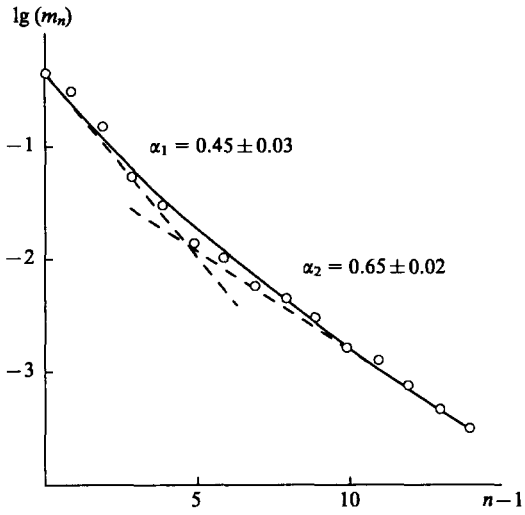


Figure 5. Molecular weight distribution for *N*-(n-alkyl)piperidines obtained in synthesis from CO, H_2, and piperidine on a reduced fused iron catalyst promoted with 5% V_2O_5:[75] circles—experimental data; curve—calculation by Eqn (19) for $x = 0.36$.

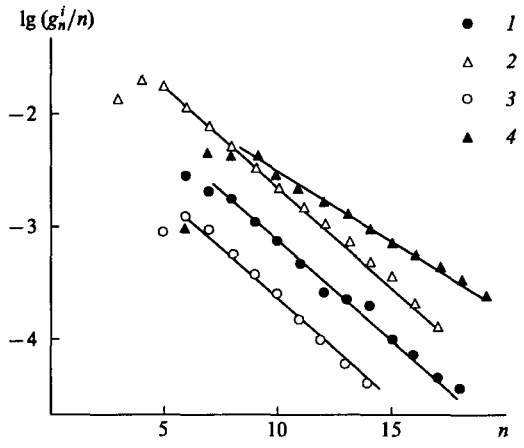


Figure 6. Molecular weight distribution for the liquid fraction of the multicomponent product of synthesis from CO and H_2 (for the conditions of the synthesis, see Table 4):[82] (*1*) α-alkenes; (*2*) n-alkanols; (*3*) n-alkyl methyl ketones; (*4*) n-alkanes; $\alpha = 0.66 \pm 0.02$ (*1–3*) and 0.77 ± 0.02 (*4*).

Evidently the change in the MWD parameters from α_1 to α_2 with increase in n from 1 to ∞ takes place continuously. The chemical significance of such continuity is associated with the simultaneous formation of the FT product independent of n, part of which is characterised by α_1 and is obtained on centres of one type, while another part is characterised by α_2 and is formed on other active centres. Eqn (19) describes MWD of type *3'* with a smaller error. As an illustration, Fig. 5 presents the MWD for *N*-n-alkylpiperidines obtained in accordance with Scheme 6 on a reduced fused iron catalyst containing 5% V_2O_5 as the promoting agent.[75] The experimental molecular weight distribution can be fitted either by two straight lines intersecting at $n = 6$, each of which is described by the Flory equation [Eqn (5)] with $\alpha_1 = 0.45 \pm 0.03$ or $\alpha_2 = 0.65 \pm 0.02$ ($\Delta = 0.20$), or by a curve corresponding to the equation

$$\lg m_n = \lg [0.36\,(0.45)^{n-1} + 0.64\,(0.65)^{n-1}].$$

The maximum standard deviation when the above equation is used for $n = 6$ is 55%, while in the range $1 < n < 15$ it is only 14%. The large error of the description of the experimental MWD by Eqn (19) in the vicinity of the break point may indicate the lack of validity of the approach used by Huff and Satterfield[60] and the inadequacy of Eqn (19) for such sections of the MWD. It is entirely likely that the type of the FT synthesis products obtained depends on n: FT products with only α_1 or α_2 are formed for $1 < n < 6$ and $n > 6$ respectively. The appearance of a break can then be associated with, for example, the steric control of the FT synthesis occurring with participation of two types of active centres of the catalyst.

4. The molecular weight distribution characteristic of cases where the parameter α diminishes with increase in n. Such MWD are also encountered in the study of hydrocarbon FT synthesis products.[21,48,51,78–80] Sometimes there is no break and the MWD reduces to type *4'*. The MWD of types *4* and *4'* arise under nonstationary conditions of the FT synthesis (in the presence of temperature and concentration gradients)[78] or for large losses in the stages involving the collection and/or analysis of low- and high-molecular-weight products.[79]

5. The molecular weight distribution in the form of several, often parallel, straight lines occurs in the study of real multicomponent FT products containing (a) only hydrocarbon components (n-alkanes, isoalkanes, α-alkenes, *cis*- and *trans*-alkenes),[53,63,64] (b) hydrocarbons and oxygen-containing compounds (n-alkanes, alkenes, alkanols, alkanals),[61,65,81] and (c) hydrocarbons and oxygen- and nitrogen-containing compounds in the case of the FT synthesis products modified by the addition of ammonia or dimethylamine (Fig. 6).[82–84] Different equations are used to describe the MWD. Some of them were examined above. Fig. 6 presents the MWD for the part of the product obtained from CO, H_2, and Me_2NH on a reduced, promoted, and fused iron catalyst (RPFIC).[82,84] It is seen from these data that Eqn (11') describes satisfactorily the experimental results.

6. The molecular weight distribution differing from the ASF distribution and not described by the Schulz or Flory equation.[2,11,20,85–89] Successful attempts to consider such MWD with the aid of the Poisson equation[90] are described in the literature:[11,88]

$$m_n = \frac{e^{-v} v^{n-1}}{(n-1)!}, \tag{20}$$

$$g_n = \frac{e^{-v} v^{n-1} n}{(n-1)!\,\bar{n}}, \tag{21}$$

where m_n and g_n are the mole and weight fractions of the FT synthesis product with n carbon atoms, v is the average number of chain propagation stages, and $\bar{n} = v + 1$ is the average degree of polymerisation.

Products obtained from CO and H_2 on Ru, Co, or Fe catalysts deposited on carriers with a high specific surface (of the order of 100 $m^2\,g^{-1}$ and above) have a type *6* distribution. The position of the maximum on the distribution curve depends on the carrier surface,[85] the maximum shifting towards low-molecular-weight synthesis products with its increase. The most probable causes of the MWD of this type are a high degree of dispersion of the catalyst particles,[87] the internal diffusion control of the chain propagation by the carrier ('the cage effect'),[87] and the nonstationary nature of the FT synthesis.

IV. The influence of the conditions in the Fischer–Tropsch synthesis on the molecular weight distribution

The catalyst as well as the conditions in the Fischer–Tropsch synthesis are known to influence the composition of the products, in particular the ratio of the hydrocarbon and oxygen-containing components.[10,11] In this section, attention is concentrated on studies which consider the influence of the conditions in the FT synthesis on the MWD. Only those investigations are analysed in which there were no effects due to the nonstationary nature of the FT synthesis, as well as those in which the parameter α was determined taking into account the experimental error, including cases where the data presented in the original papers made it possible to estimate the accuracy of the calculation of α. The temperature, pressure, the composition of the synthesis of gas and its space velocity, the type of reactor and the catalyst, the duration of the synthesis, and the addition of a third component to the mixture of CO and H_2 (modified FT synthesis) represent a list of factors (regime parameters), the effect of which on the MWD for the products will be examined below.

Temperature. The influence of temperature on the MWD has been investigated for products obtained on iron-containing heterogeneous catalysts in the gas phase in a reactor with a stationary catalyst bed[19,23] and in the liquid phase in a reactor with a stirrer and a suspended catalyst.[65,66,73] The temperature was varied from 159 to 285 °C. In all cases, α remained constant regardless of the temperature of the FT synthesis within the limits of the error of the determination. For example, in the study of Glebov et al.[23] the 'productivity' of the FT synthesis with respect to the products (hydrocarbons + oxygen-containing compounds) increased by a factor of 3.1 with increase in temperature from 159 to 180 °C, whereas the parameter α remained constant at 0.5 ± 0.1.

Table 2 presents the values of the MWD parameter α for the FT synthesis product obtained at different temperatures on iron catalysts of different composition. It is seen from the tabulated data that, when the temperature is varied in the range of ~50 °C, the MWD parameter hardly changes.

Space velocity. The influence of the space velocity of the synthesis gas on the MWD for the FT synthesis products has been frequently investigated.[19,60,65,74] It has been noted that the degree of conversion of CO changes significantly (by tens of percentage points) but the parameter α hardly varies. For example, when the space velocity of the synthesis gas ($H_2/CO = 1.3$) changes from 88 to 424 h^{-1} in FT synthesis at 269 °C in the liquid phase on a RPFIC, the degree of conversion of CO diminishes from 96% to 76%, while the MWD parameter α remains at the level of 0.67 ± 0.02.[73]

Table 2. The molecular weight distribution parameters α for the FT synthesis products at different temperatures.[65,66]

Catalyst[a]	T/°C	α	$\bar{\alpha}$
100% Fe_3O_4	285	0.61	
+ (2–3)% Al_2O_3	273	0.59	
+ (0.7–1.2)% CaO	262	0.61	0.60 ± 0.01
+ (0.5–0.8)% K_2O	251	0.60	
+ 0.4% SiO_2	239	0.60	
	231	0.62	
100% Fe_2O_3	241	0.59	
	223	0.63	
	214	0.60	0.63 ± 0.04
	199	0.64	
	188	0.68	
100% Fe_2O_3	261	0.66	
+ 0.6% K_2O	251	0.66	0.67 ± 0.01
	224	0.69	
	211	0.68	

[a] The composition of the catalyst is quoted for a nonreduced specimen.

Pressure and the H_2/CO ratio. Data concerning the influence of pressure on the MWD for the FT synthesis products have been published[8,51,67] and are contradictory. Thus, on a cobalt catalyst at 250 °C and for $H_2/CO = 3$, an increase in pressure from 1 to 7.8 atm led to a slight increase in α. However a further increase in the overall pressure to 14 atm no longer affected the MWD parameter.[51]

Ambiguous data are available also for the influence of the composition of the synthesis gas on the MWD for the FT synthesis products.[40,65,66,71] For example, when polycrystalline iron foil was used as the catalyst at 287 °C and an overall pressure of 1 atm for the ratio $H_2/O = 100$, $\alpha = 0.13$ was obtained while in the case where $H_2/CO = 4$ it amounted to 0.30.[40]

Table 3 presents the MWD parameters α for different H_2/CO ratios, different catalysts, and a degree of conversion of CO of 5%.[65,66] It is seen from the data presented that the simultaneous change in the H_2/CO ratio from 0.5 to 5 and in the overall pressure from 3 to 13 atm hardly affects the parameter α. However, we may note that the simultaneous alteration of two inde-pendent factors (H_2/CO and P_{tot}) does not permit the estimation of the influence of the H_2/CO ratio on the MWD in a pure form.

Duration of the FT synthesis. Data concerning the influence of the duration of the FT synthesis on the MWD for the products obtained have also been published.[8,23,79] It has been shown that the parameter α increases by 0.1–0.2 with increase in the synthesis time. For example, in the study of Glebov et al.[23] α

Table 3. The molecular weight distribution parameters α for the FT synthesis products corresponding to different H_2/CO ratios.

Catalyst	T/°C	P_{tot}/atm	H_2/CO	α	$\bar{\alpha}$
Fe_2O_3	212	5	4	0.58	
	212	6	2	0.64	0.64 ± 0.04
	212	8	1	0.66	
	212	12	0.5	0.67	
100% Fe_2O_3 + 6% K_2O	240	6	5	0.68	
	240	7	2.5	0.68	0.69 ± 0.01
	240	9	1.2	0.69	
	240	13	0.6	0.70	
100% Fe_3O_4 + (2–3)% Al_2O_3	248	3	0.5	0.67	
+ (0.7–1.2)% CaO + (0.5–0.8)% K_2O	248	4	1	0.66	0.64 ± 0.03
+ 0.4% SiO_2	248	6	2	0.63	
	248	10	4	0.61	

reached 0.5 ± 0.1 in the gas-phase FT synthesis in a flow reactor with a stationary RPFIC bed after 100 h, whereas after 1000 h it amounted to 0.7 ± 0.1.

Type of reactor. The results of studies on FT synthesis by different groups of investigators using a flow reactor (stationary RPFIC bed)[14,23] and a reactor with a stirrer (a suspension of RPFIC in a solvent)[19,60,65,66] demonstrated with acceptable accuracy that the type of reactor hardly affects the parameter α, which varies in the range 0.6 ± 0.1. There has been one study,[91] specially devoted to this question, in which it was shown that the values of α for the FT synthesis products obtained on the same RPFIC and under the same conditions but in reactors of two different types are similar.

Reduction of the catalyst. Reduced heterogeneous catalysts are usually employed in FT synthesis because the reduction (or activation) operation is accompanied by an increase in the rate of the FT synthesis and ultimately leads to an increase in its productivity. The influence of the RPFIC reduction time on the MWD for the FT synthesis product has been investigated.[65] As expected, the rate of the FT synthesis increases by a factor of 20 with increase in the reduction time from 0 to 92 h, while the molecular weight distribution parameter α hardly changes.

Composition of the catalysts for the FT synthesis. Heterogeneous catalysts exhibit the greatest effectiveness in the FT synthesis. Their composition exerts the greatest influence on the MWD for the FT synthesis products.[42,43,45,47,49,55,66] It is sometimes sufficient to introduce a small amount (several per cent only) of promoting additives in order to observe a change in the MWD. We shall consider such additives in greater detail.

The addition of alkali metal compounds in the form of carbonates or oxides to the prepared catalysts or in the course of their preparation frequently increases the average molecular weight of the product.[8,40,51] However, when FeB is used as the catalyst (250–270 °C), its promotion with 1%–2% of Na_2O does not affect α.[45]

Promotion of the Ru/SiO_2 catalyst with copper diminishes α. For example, the addition of 15% of copper reduces the MWD parameter from 0.55 to 0.44.[55]

The results of the study of the influence of lanthanide metals on the MWD for the FT synthesis products have been published.[43,49] When nickel catalysts are used, the addition of 1%–1.5% of lanthanum or cerium expands the range of hydrocarbon fractions obtained from C_1-C_4 to C_1-C_8, its alteration being accompanied by a significant increase in α.[49]

FT synthesis on the (5%Fe + 2%Cu)/SiO_2 catalyst at 350 °C, at a pressure of 100 atm, and for the H_2/CO = 1 ratio results in the formation of hydrocarbons and alkanols, characterised by the same value of α = 0.37. The promotion of this catalyst with 10% La under the same conditions leads to the retention of α = 0.37 in the case of alcohols, whereas in the case of hydrocarbons α increases to 0.52.[43]

So far only one instance of the influence on α of the addition of MoS_2 to catalysts based on molybdenum carbide is known.[47] For alkanols, the addition of molybdenum sulfide diminishes α from 0.31 to 0.14.

Carriers. The carrier can also affect the MWD for the FT synthesis products. A study has been made[42] of the catalyst 5%Ru + 5%Mo + 1.25%Na_2O deposited on different carriers: activated charcoal (AC), SiO_2, and Al_2O_3. It was found that the parameters α for the products obtained at 255 °C, at a pressure of 86 atm, and for the H_2/CO = 2 ratio are different on the above carriers and increase from 0.26 to 0.39 in the sequence AC < SiO_2 < Al_2O_3.

The influence of the regime parameters and the catalyst on the break on the MWD curves. As already mentioned, breaks may appear on the MWD curves for the FT synthesis products plotted in terms of the semilogarithmic variables of the Schulz or Flory equation. The question of the stability of the breaks as a function of time and of the influence on the latter of the regime parameters (temperature, pressure, etc.) arises in this connection. There are literature data concerning exclusively the type *3* MWD characterised by two values of the distribution parameter: α_1 and α_2 with $\alpha_1 < \alpha_2$ (Fig. 4).

The stability as a function of time of the break on the MWD curves obtained on a commercial (produced by the Ruhrchemie Company) deposited catalyst having the composition 100Fe : 4.3Cu : 4.1K : 25SiO_2 at 250–265 °C, at a pressure of 15 atm, and for H_2/CO = 1 over a period of 700 h has been investigated.[73] The results of tests in both a flow reactor with a stationary catalyst bed and in a stirred reactor proved to be similar. Thus, in the flow reactor, α_1 and α_2 were respectively 0.58 and 0.94 after 71 h and 0.60 and 0.88 after 427 h. In the stirred reactor, α_1 and α_2 were found to be respectively 0.57 and 0.92 after 95 h and 0.60 and 0.85 after 619 h.

Data on the MWD for the FT synthesis products, obtained using commercial catalysts produced by various companies, have been analysed[69] and in all the instances investigated the break on the MWD curve persisted throughout the period of the tests. Similar results have been published in another communication.[70]

The influence of the composition of iron-containing catalysts on the breaks on the MWD curves has been examined.[62,68]

The following catalysts were investigated: RPFIC having the composition Fe(30%–37%) + Fe_2O_3 (59%–65%) + Al_2O_3 (3%–4%) + CaO (1%–1.3%) + K_2O (0.7%–0.9%), a 10% Fe/SiO_2 deposited catalyst (the specific surface of SiO_2 was about 700 $m^2\ g^{-1}$), and a 6% ThO_2/Fe_2O_3 deposited catalyst.[68] It was established that the initial value of the distribution parameter was α = 0.61 ± 0.02 for all the products. However, after a certain time had elapsed (after 56, 30, and 14 days for the first, second, and third catalysts respectively), breaks appeared on the MWD curve at n = 11. In the range n = 1–11, we have $\alpha_1 = \alpha$, while under conditions where $n > 11$ the parameter α_2 is different for all the catalysts, reaching, for example, 0.8 for the first catalyst.

The pressure and space velocity influence the MWD with break points.[60,67] Without altering the position of the break point, their increase leads to some increase in α_2.

Modification of FT syntheses with ammonia and amines. The MWD for the FT synthesis products under conditions where a third component was added to CO and H_2 has been investigated.[44,75,76,82–84] The third component employed was NH_3,[83] Me_2NH,[82] Et_2NH,[44] and piperidine.[75,76,84] All the results were obtained on iron-containing catalysts under the conditions of gas-phase synthesis in a reactor with a stationary catalyst bed.

Thus, in the presence of the 20.4% Fe_2O_3/SiO_2 catalyst at 220 °C at a pressure of 1–10 atm and for the H_2/CO = 2–3.6 ratios, the addition of Et_2NH to the synthesis gas hardly resulted in the formation of the corresponding alkyl(diethyl)amines, the synthesis products being the usual mixture of hydrocarbons and alcohols. The molecular weight distribution parameter α for the products remained virtually constant and amounted to 0.72 for n-alkanes (0.70 in the absence of the additive) and 0.32 for n-alkanols (0.25 without the additive).[44]

Results different from those presented above were obtained in the presence of the RPFIC.[75,76,82–84] As an illustration, we shall consider in greater detail the MWD and the overall composition for the products obtained via the CO + H_2 + Me_2NH reaction (Table 4, Fig. 7).

Table 4. Composition of the products of the synthesis on a reduced, promoted, and fused iron catalyst (RPFIC).[84]

Composition of products (%)	$CO + H_2$	$CO + H_2 + Me_2NH$
n-Alkanes	26	29
α-Alkenes	9	8
n-Alkyl methyl ketones	3	3
n-Alkanols	51	18
n-Alkyl(dimethyl)amines	–	26
Unidentified components	12	16

Note. The composition of the RPFIC was 100% Fe_3O_4 + 1% V_2O_5 + 0.75% BaO for a nonreduced specimen; the Me_2NH concentration in the synthesis gas was 7 vol.%; the content of n-alkanals was less than 1%; conditions of synthesis: T = 172 °C, P_{tot} = 120 atm, H_2/CO = 4, space velocity 10^3 h^{-1}.

The data presented in Table 4 show that the addition of Me_2NH to a mixture of CO and H_2 induces the formation of n-alkyl(dimethyl)amines having the general formula $C_nH_{2n+1}Me_2N$, where $n \leqslant 17$. On the other hand, it is seen from Fig. 6 that, in terms of the semilogarithmic variables of the Schulz equation [Eqn (4′)], the linear MWD plots for alkenes, n-alkanols, and n-alkyl methyl ketones are parallel, while the distribution parameter α, calculated from the slope of the straight line, is the same for these components, amounting to 0.66 ± 0.02. However, the n-alkanes synthesised from CO and H_2 have the parameter α = 0.77 ± 0.02.

After the addition of Me_2NH to the synthesis gas (Fig. 7), the MWD parameters for alkenes, n-alkanols, and n-alkyl methyl ketones remain the same. Furthermore, the n-alkyl(dimethyl)amines formed in the presence of the above components have the same α = 0.66 ± 0.02. The MWD parameter α for n-alkanes (0.73 ± 0.02) is again different from those for the other components. The reader is referred to other communications[82–84] for a detailed analysis of the MWD for the products of the modified FT synthesis and the mechanism of their formation and here we shall only note that the introduction of Me_2NH does not affect the nature of the MWD for all the components of the product with the exception of a slight influence on the MWD for n-alkanes (α diminished from 0.77 to 0.73).

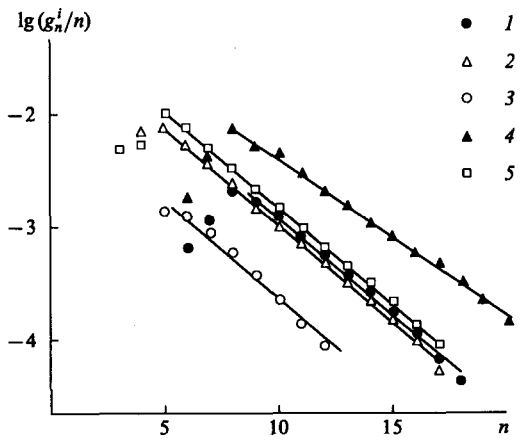


Figure 7. Molecular weight distribution for the liquid fraction of the multicomponent product of synthesis from CO, H_2, and dimethylamine (for the conditions of the synthesis, see Table 4):[82] (*1*)–(*4*) see Fig. 6; (*5*) n-alkyl(dimethyl)amines.

Zeolite-containing catalysts. New data on the MWD for the synthesis products have been obtained as a result of the study of zeolite-containing catalysts.[92,93]

Thus the catalyst having the composition 10% Fe_2O_3 + 15% MnO + 39% HY was used in the synthesis from CO and H_2 at 300–370 °C and P_{tot} = 21 atm, for a space velocity of 230 h^{-1}, and for the ratio H_2/CO = 3. The synthesis products contained C_6–C_{11} aromatic hydrocarbons which did not obey the ASF distribution. The introduction of the HY zeolite into the catalyst induced (apart from the appearance of aromatic hydrocarbons among the synthesis products) a change in the MWD for the alkanes, expressed by a shift of the break point on the MWD curve for the alkanes from n = 12 to n = 10 and was accompanied by a decrease $\Delta\alpha$ in the distribution parameter.[92] Failure of the aromatic hydrocarbons obtained in the synthesis from CO and H_2 to obey the ASF distribution was noted also in another study,[93] where the 14.7% Co/SiO_2 + ZSM-5 catalyst was used.

The deviation of the MWD for aromatic hydrocarbons from the ASF distribution has been observed also by Savel'ev et al.[94] The synthesis from CO and H_2 on an iron-containing catalyst having the composition (8.3% Fe + 4.5% K)/Al_2O_3 at 380–420 °C and P_{tot} = 1 atm, for a space velocity of 75–150 h^{-1}, and for H_2/CO = 2 yielded a product containing up to 20% of C_6–C_9 aromatic hydrocarbons apart from C_1–C_6 aliphatic hydrocarbons. On the basis of data for the MWD for the synthesis products, the authors[94] concluded that the paths leading to the formation of aliphatic and aromatic hydrocarbons are independent.

* * *

Thus the study of the MWD for the real synthetic products obtained in the FT synthesis or its modifications constitutes a vigorously developing field of research. Answers to a number of questions associated with the mechanisms of these syntheses and with the occurrence of side reactions have been obtained with the aid of the MWD. Attention has been turned to the possible hydrocondensation and hydropolymerisation character of the FT syntheses. For example, it has been possible to demonstrate that the paths leading to the formation of the main components of the product from the common intermediate in FT synthesis on the RPFIC are parallel and it has been established that the paths leading to the formation of aliphatic and aromatic hydrocarbons are independent. There is also no doubt that further improvement of highly effective analytical methods will promote the development and progress in the studies on the MWD for the products. One may claim that the study of the MWD for the FT synthesis products occupies a special place among modern methods for the investigation of the FT synthesis, such as the kinetic and isotopic methods under stationary and non-stationary conditions, spectroscopic methods applied in situ, and methods involving the organometallic analogues of the reactions of CO and H_2. The MWD method helps to obtain more complete experimental data in this interesting and promising and hitherto not fully investigated field of the synthesis of organic compounds.

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