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Schulz-Flory Equation

A mechanism for chain growth in the Fischer–Tropsch synthesis, called the "Schulz–Flory polymerization," was published in 1976 (*1*). I wish to note that a quarter of a century earlier workers at the Bureau of Mines (*2–6*) and others (*7*) described the same mechanism and the same equation. In Ref. (*1*), the "Schulz–Flory polymerization" refers to the Flory equation (*8*), describing the molecular weight distribution of polymers, as modified by Schulz (*9*).

These early schemes involved one-carbon additions usually at one end of the growing chain at the end or penultimate carbons. Addition was not permitted at tertiary carbons. Both carbon number and isomer (carbon chain structure) distributions can usually be predicted with reasonable accuracy with the growth parameters taken independent of the size and structure of the chain. Ethylsubstituted species are not produced by these growth schemes, but they were subsequently found in synthesis products. If the branching parameter f is set equal to zero, the so-called Schulz–Flory equation is obtained, and no branched species are predicted.

In the early work (*2–4*) the carbon chain distribution for a given carbon number in terms of ratios of branched to normal species are: monomethyl/normal, f or $2f$; and dimethyl/normal, f^2 or $2f^2$. The agreement with the recent data of Pichler and Schulz (*10*) for entrained iron is reasonably good, as shown for $f = 0.107$ in Table 1. Ethyl species were present in about the same amounts as the dimethyl species in

TABLE 1

Isomer (Carbon Chain) Distribution from Entrained Iron Synthesis

Carbon No.	Chain structure[a]						
	2M	3M	4M	23DM	24DM	25DM	34DM
4	0.0917[b]						
5	0.2330[c]						
6	0.2065[c]	0.1429[b]		0.0113[d]			
7	0.1891[c]	0.2845[c]		0.0306[e]	0.0069[d]		
8	0.1941[c]	0.2294[c]	0.0970[b]	0.0243[e]	0.0186[e]	0.0094[d]	0.0131[d]
9	2M + 4M 0.3659[f]	0.2166[c]		0.0218[e]	0.0140[e]		

[a] M = methyl, DM = dimethyl.
[b] Corresponds to $f = 0.107$.
[c] $2f = 0.214$.
[d] $f^2 = 0.0114$.
[e] $2f^2 = 0.0226$.
[f] $4f = 0.428$.

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this sample. One way to obtain ethyl species is to permit two-carbon and higher species, as well as one-carbon species, to add to the growing chain (*11*).

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