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Telomerization Model for Cobalt-Catalyzed Fischer–Tropsch Products

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The products from cobalt-catalyzed low-pressure Fischer–Tropsch syntheses were quantitatively analyzed for their carbon number distributions. On-line dual column chromatography measured the products up to C_{16}; off-line capillary chromatography measured the heavy products. With the exception of the C_1 to C_4 products, Schulz–Flory-type distributions were analytically demonstrated up to C_{22}. The C_2 to C_4 products were found to be nearly constant fractions of the values expected from Schulz–Flory distributions, depending little on the experimental variables. A simple model based on telomeric initiation by the primary C_2 to C_4 olefins gives a good quantitative description of the entire distribution, with the exception of the C_1 fraction.

INTRODUCTION

The products of the Fischer–Tropsch syntheses were regarded by many as polymers. Herington (*1*) suggested that the intermediate species have equal chances to grow to one carbon higher species and derived equations to describe the molecular weight distribution of the products. Product analyses by Friedel and Anderson (*2*), Pichler *et al.* (*3, 4*), and by many others have confirmed that, with some noted exceptions, the products can be described by a growth factor. The early progress in the field was reviewed by Henrici-Olivé and Olivé (*5*). They have applied the theories of step-growth polymerization of Schulz (*6*) and of Flory (*7*) to the Fischer–Tropsch synthesis. They have also shown (*5*) that the equations derived for the molecular weight distribution by Schulz (*6*) and by Flory (*7*) are nearly identical.

In recent years, there has been a renewed interest in the molecular weight distributions of the Fischer–Tropsch products. The interest was generated by reports about exceptional distributions and by the advancement of theories to account for the exceptional distributions. This research was also fueled by the desire to find ways to avoid the constraints of the Schulz–Flory distributions. The best known abnormalities in the molecular weight distribution occur in the C_1 to C_3 region; changes in the growth factor in the C_{10} to C_{12} region were also widely reported. Other types of irregularities were also described. Two papers reviewing the subject (*8, 9*) gave, among others, the following reasons that could account for the reported abnormalities in the molecular weight distributions: mass transfer limitation; olefin incorporation, especially of ethylene; different catalytic sites with different growth factors; pore size affecting growth (molecular sieve effect); non-steady-state conditions; concentration gradient and/or temperature gradient in fixed bed reactors; hot spots in the catalyst bed; artifacts associated with sampling and analyses, etc. We note that the Schulz–Flory equation does not consider temperature and concentration effects, yet these independent vari-

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ables can have an effect on the growth factor (*8*). We also focus attention to the analytical difficulties in obtaining reliable molecular weight distribution data. As pointed out by many authors (*8–10*), quantitative analyses of the products consisting of hundreds of components and ranging from gases to waxes is not a trivial task.

Our interest was a quantitative description of the molecular weight distributions obtainable over conventional cobalt catalysts in a fixed bed. The Schulz–Flory equation gives an approximate, but quantitatively unsatisfactory description. On the basis of recent reviews (*5, 11*) it appeared to us that the analytical developments are lagging behind the theoretical progress in accounting for the anomalies in the distributions. The most detailed analytical work on cobalt-based Fischer–Tropsch products was performed by Pichler *et al.* (*3, 4*) about 25 years ago. These authors introduced capillary chromatography for better resolution of the components and reported analyses up to C_{17}. Their work suggested Schulz–Flory-type distributions, with exceptions in the C_1–C_3 region and less definable deviations in the higher product range (*10*). In recent years, automated online analyses have been developed for Fischer–Tropsch products (*12*), yet we have not found reports on exhaustive product analyses and evaluations using these systems. Particularly, analytical data on cobalt-based product analyses covering the high molecular weight ends seem to be scarce. Borg and Bennett (*13*) reported data up to C_{30} that appeared to follow a Schulz–Flory-type distribution. Madon and Taylor (*14*) reported analyses from alkali-promoted, sulfur-poisoned cobalt, that have been extended up to C_{45}. This paper reported very irregular distributions in the heavy product range, often with several maxima. Pannel *et al.* have presented data up to C_{30} from La-promoted cobalt on alumina (*15*) that resembled Schulz–Flory-type distributions with noticeable irregularities. More recently, Eilers *et al.* (*16*) have reported that in the Shell Middle Distillate Synthesis, "the carbon number distributions were in close agreement with the Anderson–Schulz–Flory chain growth kinetics."

Our approach was to analyze and evaluate the entire product distribution in experiments covering a fairly broad range of conditions, with special attention to analytical quantitation. This involved a combination of analytical data from on-line analyses of the lighter products and off-line analyses of the heavy products. An evaluation of the data revealed good agreement with Schulz–Flory-type distributions with the exception of the C_1 to C_4 products. Furthermore, the C_2 to C_4 deviations were found quite "regular." These findings led to the development of a model that accounts for the deviations from the Schulz–Flory distribution and defines the distribution with the exception of C_1.

EXPERIMENTAL SECTION

All the catalysts were conventional precipitated, promoted cobalt supported on diatomaceous earth. Detailed descriptions of some of the catalysts were previously reported (*17*). The catalyst (1.0–3.3 mm in size) was charged into a 3/4″ I.D. carbon steel tube reactor containing a 1/8″ O.D. concentric thermowell. The reactor was part of an automated catalyst evaluation unit. The catalyst was activated by reduction in a hydrogen stream at 380°C. The synthesis gas, with a few exceptional experiments using higher H_2 to CO ratios, had the following composition: 17.0% CO, 34.0% H_2, and 49.0% N_2. The reactor effluents passed through a wax-trap maintained at 140–180°C to prevent condensations in the heated GC lines. Following the wax-trap, a shunt line was branched to an HP-5850 chromatograph for automated analyses. This analytical system resembled similar systems described in the literature (*12, 18*), with special attention to quantitation (*19, 20*). The growth factors (α-values) were determined from the slope of the

Schulz–Flory plots of the C_6 to C_{10} selectivities. The process conditions corresponding to the analytical data are provided in Table 1. The data presented in Tables 1 to 3 were generated after 4 to 136 days of continuous syntheses. After the wax-trap and the GC shunt, the effluents passed through an ambient trap to condense out the liquid products. Combining the contents of the wax-trap and the hydrocarbon phase of the room-temperature trap provided samples for quantitative analyses of the heavy products. During the trapping periods (usually 2–7 days), the product compositions and the α-values were monitored by on-line analyses. Only those samples were analyzed that were collected under stable conditions (i.e., no significant change occurred in the conversion, selectivities, and the growth factor). The samples evaluated in Figures 3 and 4 were obtained from a catalyst not shown in the tables, at 169 kPa, with the regular 17–34–49 feed composition, at 192 and 200°C, respectively.

The gas chromatographic analyses of the liquid hydrocarbon products combined from the two traps were performed on a Varian 3700 gas chromatograph equipped with a flame ionization detector and a split injector. A 30-m capillary column coated with SE-30 stationary phase was employed. The column oven was linearly temperature programmed from 50 to 300°C at 8°C/min after an initial hold of 2 min. Helium carrier gas was employed, and the column head pressure was maintained at 20 psig. Injection volumes were 3 μl. Injector and detector temperatures were maintained at 200 and 300°C, respectively. Five minutes after the injection, the injector temperature was raised to 300°C. For quantitation, the peak areas of the small peaks (branched paraffins) were combined with the area of the following major peak (normal paraffin) to obtain the total areas for the C_n fractions. The C_n carbon selectivities were considered to be proportional to the C_n fractions.

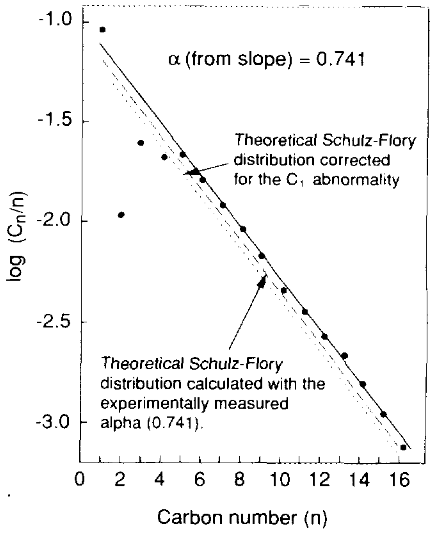

FIG. 1. Schulz–Flory plot of typical molecular weight distribution data.

RESULTS AND DISCUSSIONS

1. *On-Line Analyses of the Products up to C_{16}*

Numerous on-line analyses were performed using a variety of catalysts. These analyses yielded reproducible quantitative data for the products up to C_{16}, if condensations in the sample lines were avoided. Figure 1 gives the Schulz–Flory plot of a typical analysis. This indicates a Schulz–Flory-type distribution, as revealed by the excellent straight-line fit for the C_5 to C_{16} products. An α-value of 0.741 was derived from the slope of the straight line. The Schulz–Flory-type distribution was further indicated by the applicability of the basic equation of the step-growth polymerization (Eq. (1)) for the calculation of the C_n product mole fractions in the knowledge of the α-value and one single C_n-value.

$$\frac{C_{(n+1)}}{n+1} = \alpha \frac{C_n}{n}, \qquad (1)$$

where $C_{(n+1)}$ and C_n are the carbon selectivities of the reaction products containing n + 1 and n carbon numbers, respectively, and α is the growth factor. (The carbon selectivity to C_n is the fraction of the converted carbon monoxide ending up in C_n molecules that include both olefins and paraffins. The growth factor defines the chances of any C_n intermediate to grow to $C_{(n+1)}$.

However, the product distribution of Fig. 1 was not identical with the ideal Schulz–Flory distribution. The dashed line gives the theoretical product distribution calculated with 0.741 growth factor. It can be seen that the measured product distribution line is parallel-shifted upwards compared to the ideal Schulz–Flory line. The data of Fig. 1 also indicate that the C_2 to C_4 product selectivities were lower than anticipated. The C_5 selectivity was slightly below the measured product distribution line.

The Schulz–Flory plots of a great number of analytical data showed very similar distribution patterns to those of Fig. 1. To find out whether there is any regularity in the deviation of the C_1 to C_4 products, the data from randomly selected analyses were evaluated by calculating the extent of the deviations from the expected values.

Table 1 compares the measured and the theoretical (Schulz–Flory) methane selectivities. The measured methane selectivities were always higher than the theoretical values. Attempts to correlate the extent of the deviations with the process variables did not lead to a general correlation, apparently because too many variables can influence the methane selectivity.

The C_1 selectivities of the reaction include methane plus carbon dioxide. This latter product is formed in a side reaction (water–gas shift) and is not part of the Fischer–Tropsch synthesis products. Nev-

TABLE 1

Selected Sample Analyses, Evaluation of the C_1 Selectivities

ID No[a]	Temp. (°C)	Pressure (kPa)	α	CH_4 Selectivity		% CO_2 Selectivity Found
				Found	% of SF[b]	
1–1	196	203	0.806	6.6	174	3.1
1–2	194	203	0.776	7.0	140	3.0
1–3	194	203	0.770	7.3	138	3.0
2–1	187	107	0.758	8.9	153	1.6
2–2	196	169	0.752	8.4	140	2.1
2–3	202	169	0.725	11.4	152	2.2
3–1	196	190	0.804	8.5	224	3.9
3–2	196	210	0.808	6.8	184	3.3
3–3	195	203	0.779	9.4	192	3.8
4–1	191	155	0.791	7.9	180	5.1
4–2	202	155	0.696	10.5	115	3.4
4–3	195	155	0.786	7.0	152	4.2
5–1	191	155	0.798	7.9	193	2.0
5–2	194	155	0.780	10.8	225	2.2
5–3	193	203	0.808	8.8	218	2.2
6–1	198	155	0.713	10.1	123	2.4
6–2	198	203	0.719	10.2	131	2.7
6–3	205	245	0.745	10.7	165	3.8
7–1	207	107	0.570	28.2	157	2.6
7–2	210	162	0.637	23.4	184	4.7

[a] The first number identifies the catalyst, the second the sample.

[b] SF = the carbon selectivity calculated from the Schulz–Flory equation with the experimentally determined α-value.

TABLE 2

Evaluation of the C_2, C_3, and C_4 Selectivities

ID No[a]	% C_2 Selectivity		% C_3 Selectivity		% C_4 Selectivity	
	Found[b]	% of SFC[c]	Found	% of SFC[c]	Found	% of SFC[c]
1–1	1.8	31.7	5.8	84.6	7.7	104.5
1–2	1.9	25.9	6.2	72.6	8.0	90.5
1–3	2.1	27.4	6.6	74.5	8.4	92.4
2–1	2.3	27.4	7.2	75.5	9.2	95.5
2–2	2.3	26.3	6.6	66.8	8.5	85.5
2–3	3.0	29.5	7.9	71.5	9.9	92.7
3–1	1.6	28.5	4.5	66.6	6.2	85.6
3–2	1.4	25.3	4.5	67.0	6.3	87.1
3–3	2.0	29.0	5.6	69.4	7.5	89.5
4–1	2.0	22.0	6.0	80.8	7.6	99.6
4–2	3.5	29.0	9.8	77.8	11.6	99.3
4–3	2.0	30.0	6.2	78.9	8.0	97.1
5–1	1.6	26.3	5.1	70.0	6.5	83.8
5–2	2.1	30.6	5.8	72.2	7.3	87.4
5–3	1.8	32.8	5.2	78.2	6.4	89.4
6–1	2.9	26.2	8.2	69.2	10.0	88.7
6–2	2.9	27.3	8.0	69.8	9.7	88.2
6–3	3.1	35.3	8.1	82.4	9.9	101.4
7–1	5.8	33.5	11.9	80.3	13.4	121.7
7–1	4.7	34.5	9.7	74.5	11.9	107.6

[a] The first number identifies the catalyst, the second the sample.

[b] The C_2 product was >95% ethane, with a little ethylene.

[c] SFC = the carbon selectivity calculated from the Schulz–Flory equation with the experimentally determined α-value, and corrected for the "C_1 abnormalities."

ertheless, the CO_2 selectivities are shown in Table 1 because of their impact on the material balance and hence on the absolute values of the hydrocarbon selectivities. The methane selectivity in excess of the theoretical value and the CO_2 selectivity will reduce the carbon selectivity values of the C_2+ products formed by Schulz–Flory-type chain-growth kinetics. Since these "abnormalities" of the C_1 selectivities were analytically measured, it was possible to correct the theoretical Schulz–Flory distributions of the C_2+ products to provide a carbon-based material balance. This is illustrated in Fig. 1. It can be seen that the "corrected theoretical" distribution is parallel shifted downwards from the theoretical Schulz–Flory line. The corrected theoretical C_2 to C_4 selectivities served as a basis for evaluating the analytically found C_2 to C_4 selectivities in Table 2.

The C_2 selectivities were around 29% of the Schulz–Flory values corrected for the C_1 abnormalities (see Table 2). The constancy of the deviations is remarkable, considering the great variety of the experimental conditions (see Table 1), encompassing analyses of products with α ranging from 0.570 to 0.808. A statistical analysis of the data gave a standard deviation of 0.03 from the averaged 0.29. This standard deviation value is higher than the standard deviation of the GC analyses (*19*), suggesting that the experimental variables have contributed to the scatter. Yet we did not find a satisfactory correlation with a single variable.

The data of Table 2 indicate that the C_3 and C_4 selectivities were close to 0.74 and

TABLE 3

The Influence of the H_2 to CO Feed Ratio and of the Temperature on the C_2 to C_4 Selectivities

ID No.[b]	Temp. (°C)	α	Found selectivities, in % of the SFC[a] values		
			C_2	C_3	C_4
4–4[c]	197	0.693	32.3	79.1	100.4
5–4[d]	195	0.771	39.1	74.1	90.3
5–5[d]	191	0.787	44.6	78.4	91.8
5–6[d]	183	0.801	57.1	86.9	92.6
5–7[d]	194	0.762	46.9	82.2	96.8

[a] See Table 2 for the meaning of SFC.

[b] The first number identifies the catalyst, the second the sample.

[c] With 2.9 H_2 to CO feed ratio, at 155 kPa.

[d] With 2.5 H_2 to CO feed ratio, at 203 kPa.

0.94 fractions, respectively, of the expected selectivities. Again, there was some scatter in the data around the averaged values. The standard deviations were 0.05 and 0.09, respectively. Although the absolute standard deviation increased with the carbon number, the relative error changed little. Again, no single experimental variable was found to correlate with the scatter.

We have tried an experimental approach to demonstrate which of the variables play a role in influencing the extent of variation in the C_2 to C_4 selectivities. Table 3 shows that both the H_2 to CO feed ratio and the reaction temperature can have an effect. In the case of Catalyst 4, an increase in the H_2 to CO feed ratio to 2.9 only slightly affected the extent of deviations in the C_2 to C_4 selectivities. (Compare 4–4 in Table 3 to 4–2 and 4–3 in Tables 1 and 2.) However, in the case of Catalyst 5, upon increasing the H_2 to CO feed ratio from 2.0 to 2.5, the deviation in the C_2 selectivity was greatly influenced (compare 5–4 and 5–5 in Table 3 to 5–2 and 5–1, respectively, in Tables 1 and 2). Decreasing the reaction temperature caused further changes, particularly in the C_2 selectivity (see Table 3). Returning to 194°C, the C_2 to C_4 selectivities and the growth factor returned nearly to the original values. These results illustrate that the C_2 to C_4 selectivities were considerably affected by the H_2 to CO ratio of the feed.

2. *Analyses of the Heavy Product Fractions*

A typical chromatogram of the condensed hydrocarbons is shown in Fig. 2. The product distributions go through a maximum, because the lower boiling components did not condense or incompletely condensed. We have assumed a 100% recovery of the liquids for the declining portion of the product distribution starting with a carbon number that is five carbons higher than the maximal. At this carbon number, the carbon selectivity was taken identical with that determined for the same carbon number by graphic extrapolation of the C_6 to C_{10} data in a Schulz–Flory plot like Fig. 1. This way the quantities of the liquid samples were quantitatively linked to the carbon selectivities of the synthesis. Figures 3 and 4 compare the extrapolated Schulz–Flory selectivities (solid line) with the experimentally determined selectivities. Analyses of additional liquid samples showed analogous patterns.

An examination of Figs. 3 and 4 reveals that the agreement between the anticipated and the experimentally found values is ex-

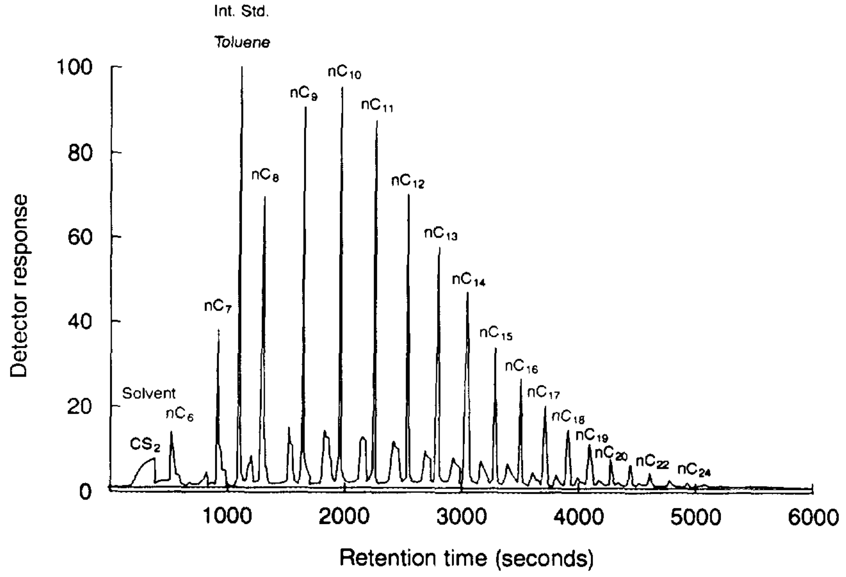

FIG. 2. Capillary chromatogram of the condensed hydrocarbon fraction.

cellent up to about C_{22} carbon number. At the high molecular weight ends, the experimentally determined values were always lower than the predicted values. Just before the experimental data dipped below the theoretical line, a few data points appeared to be slightly above the theoretical line.

The data clearly indicate, that, at least to about C_{22}, the products follow a Schulz–Flory-type distribution. It can be seen in Figs. 3 and 4 that the deviations at the higher carbon numbers are at the hundredth of the product percent level, that is quantitatively insignificant. Furthermore, for products boiling above 330°C (i.e., for $>C_{19}$), our GC measurements may be biased too low because of incomplete vaporizations using our injection techniques. We also wish to point out that there may be an additional reason for the low values of the analytical data at high carbon numbers. It is well known that the catalyst pores retain the heavy products (waxes). Wax retention by the catalyst could also account for the lower than theoretical concentrations of the high carbon number products. If the catalyst pores were

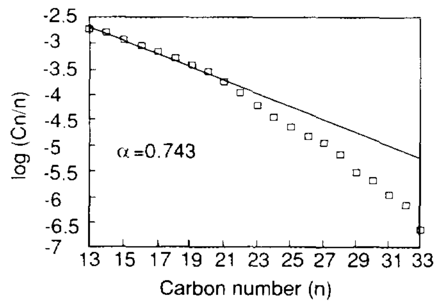

FIG. 3. Calculated (solid line) and experimentally found (squares) distributions of the heavy fractions.

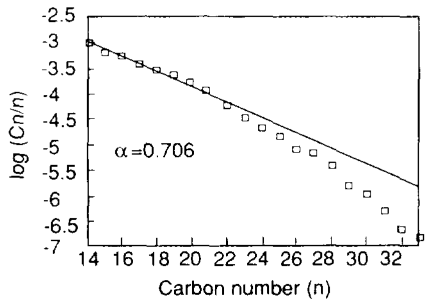

FIG. 4. Calculated (solid line) and experimentally found (squares) distributions of the heavy fractions.

not filled yet, the heavy ends may be missing from the collected samples. If the catalyst pores were already filled, the heavy ends still are expected to be retained by the catalyst with the simultaneous release from the pores of some lower carbon number products. In Figs. 3 and 4, a few contiguous data points sightly above the theoretical line may be explained by this interpretation.

3. The Telomerization Model

A wealth of information has been accumulated in the literature on the subject. We combine this information with our analytical observations to develop a model that can mathematically describe the molecular weight distributions. The basic concepts of the model are summarized below:

1. The primary products of the synthesis are formed in the amounts predicted by the polymerization rules. The primary products are defined by a single growth factor. The only exception to the rule occurs at the C_1 level; the methane selectivity is not predictable.

2. The deviations from the Schulz–Flory distribution are due to secondary reactions of the primary products. It is well known that olefins, alcohols, and aldehydes can initiate new chains and be incorporated into the final products (*5, 11, 21–27*). If a new chain is initiated by the primary product, it can be regarded as a telomerization. Hence we call the model a telomerization model. It is also well known from the literature that telomerization is not the only secondary reaction: hydrogenation and isomerization of the olefins, branching and hydrogenolyses of C–C bonds also occur. With the exception of the C–C bond hydrogenolyses, these reactions do not affect the carbon number distribution at all. Furthermore, our experimental data did not reveal any discrepancies in the carbon number distributions that could possibly originate from C–C bond hydrogenolyses. Hence none of these secondary reactions will be considered for the model. Furthermore, the considerations will be restricted to the telomerization of ethylene, propylene, and butylene, because these were the only reactions found to impact significantly the carbon number distributions. Based on our findings, it is assumed that the telomerization occurs with the same growth factor as the "polymerization" of the synthesis gas. Finally, the model assumes that the ratio of the telomerized and the initially formed C_2 to C_4 products is constant.

3. The model assumes that only hydrocarbons form in the reaction and that oxygenate formation is negligible. This was confirmed by showing that oxygenates form in less than 0.01 carbon selectivity in our system (*20*). The model requires the measurement of the methane and carbon dioxide selectivities (that provide a combined C_1 selectivity) and of the growth factor, to describe the distribution and to provide a material balance.

4. The model is based on data generated in fixed bed reactors. In fixed beds, feed concentration gradients are known to exist that may result in a continuous decrease in the value of the growth factor along the bed length. Furthermore, isothermal operation of fixed-bed Fischer–Tropsch reactors is practically impossible, and we have to anticipate some changes in the growth factor due to temperature gradients. However, the composition of the reactor effluent still can be described by a single growth factor, if the temperature and the concentration gradients are continuous and not excessive. This is an averaged growth factor characteristic for the reactor conditions.

The carbon number distribution for the C_5+ products is described by

$$\text{for } n > 4 \quad C_n = (1 + F)(\ln^2\alpha)n\alpha^n, \tag{2}$$

where

$$F = \frac{\sum_{n=1}^{4} (n\alpha^n \ln^2\alpha - C_n)}{1 - \sum_{n=1}^{4} n\alpha^n(\ln^2\alpha)}.$$

The fraction *F* quantifies the parallel shift of the experimental measurements to the right of the Schulz–Flory theoretical distribution (Fig. 1). The numerator of F is equal to the net departure of the measured selectivities from the theoretical for carbon numbers less than 5. The denominator of F is equal to the sum of all Schulz–Flory selectivities for carbon numbers greater than 4. Thus, the extent to which the low carbon number primary products initiate new chains, and the growth factor, will determine the magnitude of F. Since for our range of experimental conditions the ratio of secondary initiation of new chains appears to be relatively constant for carbon numbers two through four, we can obtain an empirical expression which quantifies the net C_2, C_3, and C_4 selectivities after reductions by the secondary reactions,

$$\text{for } 1 < n < 5 \quad C_n = A_n(1 - F_1)(\ln^2\alpha)n\alpha^n,$$

where

$$F_1 = \frac{C_1 - \alpha(\ln^2\alpha)}{1 - \alpha(\ln^2\alpha)}$$

$$A_2 = 0.29$$

$$A_3 = 0.74$$

$$A_4 = 0.94.$$

Because of the quantity of methane and carbon dioxide found which is in excess of the quantity of C_1 expected from the Schulz–Flory distribution, a factor is used to adjust the Schulz–Flory expression for this effect in order to evaluate the C_2, C_3, and C_4 selectivities. This factor, F_1, quantifies the parallel shift of the experimental measurements to the left of the Schulz–Flory theoretical distribution for carbon numbers 2, 3, and 4. The numerator of F_1 is equal to the net departure of the measured C_1 selectivity from the theoretical. The denominator of F_1 is equal to the sum of all theoretical selectivities for carbon numbers greater than 1. The coefficients A_2, A_3, and A_4 were empirically determined by ratioing the measurements of C_2, C_3, and C_4 to the theoretical selectivities after correction by the factor F_1.

Thus, if the selectivity for the C_1's and the growth factor are known, the selectivities for all other carbon numbers can be determined by these mathematical expressions. Also from these expressions, we see our shift factor, F, ultimately depends only on the growth factor and the C_1 selectivity.

The polymerization literature has cast some doubt on the validity of the assumption that the growth factor remains constant with increasing molecular weights (*28*). In our analyses of the molecular weight distributions, the growth factor appeared to remain constant. However, it should be considered that, in the present case, we are dealing with oligomers rather than high molecular weight polymers.

It is interesting to note that only the most reactive members of the olefin series were found to incorporate into the product by initiating a new chain. Furthermore, the efficiency of the initiation was found to decrease with increasing carbon number as revealed by the 0.71, 0.24, and 0.06 incorporation factors for ethylene, propylene, and butylene, respectively. Carbon-13 tracer work by Schulz *et al.* (*24*) has shown that even hexadecene can initiate new chains, even though it preferentially hydrogenates to paraffins or degrades to lower carbon products (*24*). While degradation could potentially impact the carbon number distributions, our analyses did not reveal measurable signs of such reactions in our syntheses.

The readsorption of propylene and of 1-butene can give two isomeric intermediates. The isomers with metal-secondary carbon bonds would lead to 2-methyl and 3-methyl branches, respectively, on further growth. Our model would predict that the amount of 3- and 4-methyl branches would depend on the growth factor. Only the maximal possible amount of branches can be predicted, assuming 100% secondary carbon attachment to the cobalt upon readsorption. For example, with 0.70 growth factor, max.

TABLE 4

Calculated and Experimental C_2 to C_4 Selectivities

α	% C_1 Selectivity (CH_4 + CO_2) Experimental	% Carbon Selectivities to C_2 to C_4 Products		
		Schulz–Flory model	Telomerization model	Experimental
0.64	28.1	37.7	24.0	26.3
0.70	13.9	36.3	23.8	24.9
0.75	10.5	28.5	19.2	17.4
0.80	12.4	19.6	13.4	12.3

7.2% 3- and 4-methyl branches were calculated. Not even this inflated value could account for the amounts of the branched products known to be present and to have internal branches also (*4, 11*). Indeed, based on his exhaustive studies on branching, R. B. Anderson did not consider olefin incorporation as a major source of branching (*11*).

In Table 4, we illustrate the salient differences between the telomerization model and the Schulz–Flory model. Specifically, the C_2 to C_4 product yields are compared at several different α-values. In a future publication we wish to illustrate how these developments have led to the determinations of the growth factor from the measurement of the C_2 selectivity.

The scope and limitations of the telomerization model have not been fully examined. It was found to be valid for cobalt-based products in hundreds of analyses within confined experimental regimes. We would anticipate that the model should be valid under much broader experimental ranges (e.g., at high pressures or using undiluted synthesis gas), but this will need verification. In principle, the model should be valid even if oxygenates formed in substantial quantities, with appropriate adjustment of the formula.

However, the model is not applicable for Fisher–Tropsch products obtained over Fe- or Ru-based catalysts. This becomes apparent after reviewing the relevant literature. Numerous olefin cofeeding studies indicated (*25*) that olefins incorporate into the synthesis products over Fe and Ru, as well as Co. Molecular weight distribution data (Schulz–Flory plots) can provide quantitative information about the extent of olefin incorporation. A dip at C_2 or C_3 below the Schulz–Flory line indicates the incorporation by telomerization of ethylene or propylene, respectively. Examination of a number of Schulz–Flory plots reported with Fe catalysts (*29, 30*) suggests that some ethylene can incorporate over Fe, but practically no propylene. Due to their lower reactivity, higher olefin incorporation would not be anticipated. Hence we conclude that olefin telomerization is not a significant side reaction over Fe. Similar conclusions were drawn by Hanlon and Satterfield (*31*) and by Schulz *et al.* (*24*) on the basis of cofeeding studies. Based on similar studies Davis *et al.* (*32*) reported 10% ethylene incorporation over Fe; this is a low value, indeed, compared to our 71% incorporation over Co. Recently two papers by Iglesia *et al.* (*33*) and by Madon *et al.* (*34*) described an olefin incorporation model for Ru/TiO_2 catalyst. The primary olefins were reported to initiate new polymerization chains after transport-enhanced readsorptions, resulting in increasing growth factor with increasing chain length. Furthermore, changes were demonstrated in the product distribution, the 1-olefin content and the paraffin content with increasing residence time. According to the model, all the olefins initiate telomerization, and telomerization is preferred over olefin hydrogenation. In a very recent paper (*35*) their model was also extended to Co catalyst. Their molecular weight data obtained on various supported Co catalysts—different in preparation and testing conditions from ours—differed substantially from our molecular weight distribution results. At this point the cause of the differences can not be defined.

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