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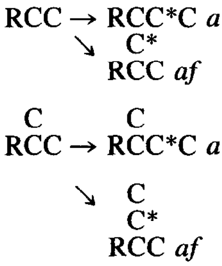
# McCandlish Chain Growth Scheme

Recently McCandlish (*1*) presented an interesting chain growth scheme, MCG, for the Fischer–Tropsch synthesis, FTS, involving stepwise addition of methylene. Methylene adds to a "naked" surface carbon to yield a surface-bonded vinylidene; this species and its higher homologs are important intermediates. Methylene now adds to the C═C bond to form a surface-bonded cyclopropylidene. The three-member ring can split in two ways to yield two vinylidenes and two products after hydrogenation. The overall reaction may be represented by reactions



$$\mathrm{RCC} \rightarrow \mathrm{RCC^{*}C}\ a \tag{1}$$
$$\searrow\ \mathrm{R\overset{C^{*}}{C}C}\ af \tag{2}$$
$$\mathrm{R\overset{C}{C}C} \rightarrow \mathrm{R\overset{C}{C}C^{*}C}\ a \tag{3}$$
$$\searrow\ \mathrm{R\overset{\overset{C}{C^{*}}}{C}C}\ af \tag{4}$$

where the asterisks represent the last carbon added to the chain, and $a$ and $f$ are constants that are independent of chain length or structure. The parameters in Eqs. (1) to (4) represent molar ratios of species found in the synthesis products, e.g., for Eq. (1) $a$ equals the moles of RCCC divided by moles of RCC. Steps 1, 2, and 3 occur in the same way in Anderson's simple chain growth scheme (*2, 3*), SCG. Step 4 may lead to the production of ethyl-, propyl-, and higher-alkyl-substituted chains.

Also the same carbon remains attached to the catalyst throughout the growth process, a feature that can be tested experimentally. This feature decreases the number and complexity of all of the steps needed for a continuous process.

The purpose of this note is to show that the MCG scheme works well in fitting isomer distributions and to extend the MCG to $C_{17}$. As will be shown, the MCG improves the agreement between predicted and observed values, compared with SCG, but MCG often undercorrects, e..g., for 3-methyl isomers. On this basis a modified McCandlish scheme, MM, in which the growth parameter for step 4 was taken as $ag$ was also tested. Table 1 presents parameters for the isomer distribution to $C_{17}$ for MCG and MM schemes. The parameters for MCG are obtained by setting $f = g$. Terms representing species which have undergone more than three branching steps were ignored. The parameters in Table 1 predict the ratio of a branched isomer to the normal species in a given carbon-number fraction. These parameters were derived by a "longhand" method from the reaction network defined by Eqs. (1) to (4). A substantial portion of the network is not affected by Eq. (4), and these species have the same constants as obtained for SCG.

The three growth schemes were applied to data of Achtsnit (*4*) from fixed-bed cobalt synthesis and to those of Pichler *et al.* (*5*) for fixed-bed cobalt and entrained iron. These excellent analyses were made on hydrogenated FTS products, i.e., olefins were converted to paraffins. The data give the amount of a particular carbon chain present in the hydrocarbons. For the SCG and MCG schemes the best value of $f$ was obtained by adjusting $f$ to minimize the residual sum of squares of observed minus predicted amounts. Because SCG does not predict ethyl-substituted chains, ratios for ethyl species and mixtures containing them were excluded from the sum of squares. The constants for MM method were evalu-

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TABLE 1

Constants for Original and Modified McCandlish Scheme

| Species | 1st Occurrence | Predicted quantity[a] | | | |
|---|---|---|---|---|---|
| | | 1st Occurrence | 2nd Occurrence | 3rd Occurrence | 4th Occurrence |
| 2M | C4 | $f$ | $2f + fg$ | $2f + fg^2$ | $2f^b$ |
| 3M | C6 | $f + 2fg$ | $2f + 2fg + 2fg^2$ | $2f + 2fg^b$ | |
| 4M | C8 | $f + 2fg^2$ | $2f + 2fg^{2b}$ | | |
| 5, 6, 7, 8M | C10, 12, 14, 16 | $f$ | $2f^b$ | | |
| 2-3, 2-4 . . . 2-9 DM | C6, 7, . . . , 12 | $f^2$ | $2f^2 + 2f^2g$ | $2f^{2b}$ | |
| 3-4, 3-5, 3-6, 3-7DM | C8, 9, 10, 11 | $f^2 + 2f^2g$ | $2f^2 + 2f^2g^b$ | | |
| 3E | C7 | $fg$ | $2fg + fg^2$ | $2fg^b$ | |
| 4E | C9 | $fg + 2fg^2$ | $2fg + 2fg^{2b}$ | | |
| 5E | C11 | $fg$ | $2fg^b$ | | |

[a] If $f = g$, the unmodified McCandlish scheme is obtained.

[b] Predicted amount remains constant at this value for higher carbon numbers.

ated using a least-squares nonlinear estimation procedure based on Marquardt's compromise. Some of the SCG evaluations were made on a smaller number of data points than those of MCG and MM; therefore, the residual sum of squares is given per data point.

Table 2 presents the values of the constants $f$ and $g$ for the three schemes and the residual sum of squares per point. MCG was always better than SCG and MM better than MCG. The value of $g$ of MM was often large, 3 to 10 times that of $f$. Because MM has one more parameter than MCG an F-test was made to determine whether MM was significantly better than MCG; the difference of the residual sums of squares of MM and MCG were compared with the estimated variance of MM. These results are also given in Table 2.

To illustrate the ability of the growth schemes to predict isomer data we have chosen as typical the $C_{10}$ and $C_{12}$ fractions of the Pichler *et al.* (*5*) data as given in Table 3. These data provide an extension of those given by McCandlish (*1*) for $C_4$ to $C_9$; however, the parameters for data in Tables 2 and 3 were optimized over the range $C_4$ to

TABLE 2

| Syn. temp. (°C) | Feed ratio $H_2/CO$ | Growth scheme | Parameters $f$ | Parameters $g$ | Residual sum of squares per point × $10^5$ |
|---|---|---|---|---|---|
| A. Data of Achtsnit (*4*) for Fixed-Bed Cobalt for $C_4$ to $C_{13}$ | | | | | |
| 187 | 1 | SCG | 0.0420 | — | 22 |
| | | MCG | 0.0417 | — | 19 |
| | | MM | 0.0381 | 0.3104 | 10[a] |
| 187 | 2 | SCG | 0.0768 | — | 109 |
| | | MCG | 0.0756 | — | 94 |
| | | MM | 0.0703 | 0.2842 | 78[b] |
| 171 | 2 | SCG | 0.0206 | — | 9 |
| | | MCG | 0.0205 | — | 8 |
| | | MM | 0.0184 | 0.3473 | 5[a] |
| 190 | 2 | SCG | 0.0537 | — | 88 |
| | | MCG | 0.0531 | — | 82 |
| | | MM | 0.0491 | 0.2849 | 71[c] |
| B. Data of Pichler *et al.* (*5*), $C_4$ to $C_{17}$ | | | | | |
| Catalyst | | Growth scheme | Parameters $f$ | Parameters $g$ | Residual sum of squares per point × $10^5$ |
| Fixed-bed cobalt | | SCG | 0.0825 | — | 62 |
| | | MCG | 0.0809 | — | 54 |
| | | MM | 0.0814 | 0.0593 | 54[c] |
| Entrained iron | | SCG | 0.0913 | — | 81 |
| | | MCG | 0.0903 | — | 59 |
| | | MM | 0.0863 | 0.2235 | 46[a] |

[a] Extra parameter gives significant improvement at 99% confidence level.

[b] Extra parameter gives significant improvement at 95% confidence level.

[c] Extra parameter does not give significant improvement.

TABLE 3

Comparison of Chain Growth Schemes

| Isomer | | Ratio of branched to normal isomers | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Fixed-bed cobalt[a] | | | | Entrained iron[a] | | | |
| | | Expt. | SCG | McCandlish | McCandlish modified | Expt. | SCG | McCandlish | McCandlish modified |
| | | | | A. Decane | | | | | |
| Monomethyls | 2 | 0.131 | | 0.162 | 0.163 | 0.162 | | 0.181 | 0.173 |
| | 3 | 0.171 | 0.165 | 0.175 | 0.173 | 0.196 | 0.183 | 0.197 | 0.211 |
| | 4 | 0.172 | | 0.163 | 0.163 | 0.168 | | 0.182 | 0.181 |
| | 5 | 0.083 | 0.083 | 0.081 | 0.081 | 0.080 | 0.091 | 0.090 | 0.086 |
| Dimethyls | 24 | 0.0066 | 0.014 | 0.013 | 0.013 | 0.012 | 0.017 | 0.016 | 0.015 |
| | 25 + 35 | 0.025 | 0.027 | 0.027 | 0.027 | 0.036 | 0.033 | 0.034 | 0.033 |
| | 26 | 0.010 | 0.014 | 0.014 | 0.014 | 0.030 | 0.017 | 0.018 | 0.018 |
| | 27 | 0.0033 | 0.0068 | 0.0065 | 0.0066 | 0.014 | 0.0083 | 0.0082 | 0.0074 |
| | 36 | 0.0033 | 0.0068 | 0.0076 | 0.0074 | 0.020 | 0.0083 | 0.0096 | 0.011 |
| Ethyls | 3 | 0.017 | — | 0.013 | 0.010 | 0.022 | — | 0.016 | 0.039 |
| | 4 + 23DM + 34DM | 0.035 | — | 0.041 | 0.038 | 0.068 | — | 0.052 | 0.080 |
| | | | | B. Dodecane | | | | | |
| Monomethyls | 2 | 0.121 | | 0.162 | 0.163 | 0.161 | | 0.181 | 0.173 |
| | 3 | 0.174 | 0.165 | 0.175 | 0.173 | 0.195 | 0.183 | 0.197 | 0.211 |
| | 4 | 0.165 | | 0.163 | 0.163 | 0.158 | | 0.182 | 0.181 |
| | 5 | 0.154 | | 0.162 | 0.163 | 0.153 | | 0.181 | 0.173 |
| | 6 | 0.076 | 0.083 | 0.081 | 0.081 | 0.084 | 0.0913 | 0.090 | 0.086 |
| Dimethyls | 24 | 0.0018 | 0.014 | 0.013 | 0.013 | 0.047 | 0.017 | 0.016 | 0.015 |
| | 25 + 35 + 26 | 0.024 | 0.041 | 0.040 | 0.041 | 0.047 | 0.050 | 0.050 | 0.048 |
| | 27 | 0.011 | 0.014 | 0.013 | 0.013 | 0.020 | 0.017 | 0.016 | 0.015 |
| | 28 | 0.013 | 0.014 | 0.014 | 0.014 | 0.035 | 0.017 | 0.018 | 0.018 |
| | 29 + 37 | 0.016 | 0.020 | 0.021 | 0.021 | 0.040 | 0.025 | 0.026 | 0.026 |
| | 36 | 0.0091 | 0.014 | 0.014 | 0.014 | 0.0022 | 0.017 | 0.018 | 0.018 |
| | 38 | 0.0036 | 0.0068 | 0.0076 | 0.010 | 0.017 | 0.0083 | 0.0096 | 0.011 |
| Ethyls | 3 | 0.018 | — | 0.013 | 0.010 | 0.020 | — | 0.016 | 0.039 |
| | 4 | 0.016 | — | 0.014 | 0.010 | 0.062 | — | 0.018 | 0.047 |
| | 5 | 0.0091 | — | 0.013 | 0.010 | 0.040 | — | 0.016 | 0.039 |
| | | | | C. Values of parameters for $C_4$ to $C_{17}$ | | | | | |
| | $f$ | — | 0.0825 | 0.0809 | 0.0814 | — | 0.0913 | 0.0903 | 0.0863 |
| | $g$ | | | | 0.0593 | | | | 0.2235 |

[a] From Ref. (5).

$C_{17}$, and are different than those used by McCandlish (*1*), i.e., 0.0903 vs 0.1008 for Fe and 0.0809 vs 0.0827 for Co.

A fourth scheme was derived by permitting also a 1,2 shift involving ethyl and larger groups. This reaction step leads to straight-chain growth according to

$$\mathrm{RCC} \rightarrow \mathrm{RC^{*}CC}\ af \tag{5}$$

$$\mathrm{R\overset{C}{C}C} \rightarrow \mathrm{RC^{*}\overset{C}{C}C}\ af \tag{6}$$

where the asterisk denotes the last carbon added. These steps have also been assigned the constant $af$. This scheme was slightly better than MCG, but the expressions for the isomers were complicated and will not be presented.

We conclude that the McCandlish mechanism (*1*) is a significant advance, providing a complete reaction scheme consistent with modern chemistry and a two-constant ($a$ and $f$) system for predicting product distributions with moderate accuracy at least up to $C_{17}$. If addition according to Eq. (4) is assigned a separate constant $g$, the agreement between predicted and observed data usually increases substantially. However, the values of $g$ are often large, 0.2 to 0.3. We also note that Eqs. (1) to (4) provide a good description of the products of FTS, and that any other proposed reaction scheme should be consistent with the overall restrictions of these growth steps. In addition these growth schemes also predict the carbon-number distribution reasonably (*6*).

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