Appendix II

Solution of the differential equations describing chain growth during Fischer-Tropsch Synthesis

The solutions for the differential equations that describe the chain growth model used in Chapter IV are derived in this Appendix. The starting point is the equations (eqn.1 and 3 in Chapter IV) for the fractional label incorporation in the monomer pool and in each of the C_n pools that are the precursors to the hydrocarbon products of chain length n. F_i is the fractional label content of pool i on the surface; τ_m is the lifetime of the monomer pool and τ is the lifetime of each of the C_n surface pools.

$$\frac{d\,F_m(t)}{dt} = \frac{1 - F_m(t)}{\tau_m} \qquad \text{.......} \quad (1)$$

$$\frac{d\,F_n(t)}{dt} = \frac{\dfrac{(n-1)F_{n-1}(t) + F_m(t)}{n} - F_n(t)}{\tau} \qquad \text{for } n = 1,n \text{ ....} \quad (2)$$

Initial and Boundary conditions:

1. The F curves for the monomer and all the C_n pools start at 0 at t =0; i. e., $F_m(t=0) = F_i(t=0) = 0$, where i = 1, n.
2. At t = ∞, all F curves have reached steady state and are equal to 1.0

Laplace transforms of the first-order differential equations 1 and 2 are used to obtain solutions for $F_n(t)$. The Laplace transform

(L.T.) of $F_i(t)$ will be represented as $f_i(s)$.

Taking the L.T. of equation 1 gives:

$$sf_m(s) - F_m(0) = \frac{\left(\frac{1}{s} - f_m(s)\right)}{\tau_m} \qquad \text{......} \quad (3)$$

From the initial condition for F_m, $F_m(0) = 0$; so this can be simplified to give

$$f_m(s) = \frac{1}{s\,\tau_m\,(s + \frac{1}{\tau_m})} \qquad \text{......} \quad (3')$$

This expression now yields the solution that

$$F_m(t) = 1.0 - \exp\left(\frac{-t}{\tau_m}\right) \qquad \text{........} \quad (4)$$

Taking the L.T. of equation 2 , we get:

$$sf_n(s) - F_n(0) = \frac{(n-1)}{n\tau} f_{n-1}(s) + \frac{1}{n\tau} f_b(s) - \frac{f_n(s)}{\tau} \qquad \text{......} \quad (5)$$

Again, using the initial condition that $F_n(0) = 0$, this yields:

$$f_n(s) = \frac{1}{n\tau(s+\frac{1}{\tau})}\left[f_b(s) + (n-1)\, f_{n-1}(s)\right] \qquad \text{......} \quad (5')$$

The L.T. of each pool depends on the L.T. of the previous pool in this set of recurring relationships as well as $f_b(s)$, except for the expression for $f_1(s)$ which only involves $f_b(s)$. From equation 5',

$$f_1(s) = \frac{1}{\tau(s+\frac{1}{\tau})}\left[f_b(s)\right] \qquad \text{......} \quad (6)$$

Now, this expression for $f_1(s)$ can be used with equation 5' to yield an expression for $f_2(s)$ and so on; ultimately, this results in the following expression for $f_n(s)$:

$$f_n(s) = \frac{f_b(s)}{n}\left[\frac{1}{\tau(s+\frac{1}{\tau})} + \frac{1}{\tau^2(s+\frac{1}{\tau})^2} + \dots \frac{1}{\tau^n(s+\frac{1}{\tau})^n}\right] \qquad \dots\dots (7)$$

The inverse transform of this expression will give the solution $F_n(t)$. Since all the terms can be expressed by a general expression for the ith term, the ith term of the above expression is inverted; the summation of this for all terms from i=1 to i=n then yields $F_n(t)$. The ith term in the expansion is:

$$f_i(s) = \frac{f_b(s)}{n}\left[\frac{1}{\tau^i(s+\frac{1}{\tau})^i}\right]$$

To get the L^{-1} or inverse L.T. of this term, use is made of the convolution theorem (1), which states:

If $f(s) = g(s)h(s)$, and $L^{-1}[g(s)] = G(t)$ and $L^{-1}[h(s)] = H(t)$,

$$F(t) = \int_0^t G(u)H(t-u)du \qquad \dots\dots (8)$$

(where $F(t) = L^{-1}[f(s)]$)

Also, from L.T. tables, the following inverse transform is obtained:

$$L^{-1}\left[\frac{1}{(s-a)^i}\right] = \frac{1}{(i-1)!}t^{i-1}\exp(at) \qquad \dots\dots (9)$$

Using eqns. 4, 8 and 9,

$$L^{-1}[\text{ith term}] = \frac{1}{n\tau^i(i-1)!}\int_0^t u^{i-1}\exp(\frac{-u}{\tau})(1-\exp(\frac{-(t-u)}{\tau_m}))du \qquad \dots\dots (10)$$

The expression can be evaluated using integral tables (2) to give:

$$L^{-1}[\text{ith term}] = \frac{1}{n}\{1 + \exp(\frac{-t}{\tau_m})(-1)^{i-1}(\frac{\tau_m}{\tau-\tau_m})^i + \frac{\exp(\frac{-t}{\tau})}{\tau^i}\sum_{r=0}^{i-1}\frac{t^{i-r-1}\tau^{r+1}}{(i-r-1)!}((\frac{-\tau_m}{\tau-\tau_m})^{r+1}-1)\} \qquad \dots\dots (11)$$

From eqn. 11, $F_n(t)$ can be evaluated:

$$F_n(t) = \sum_{i=1}^{n} [L^{-1}(\text{ith term})]$$

$$F_n(t) = 1.0 + \left(\frac{\exp(-\frac{t}{\tau_m})}{n}\right)\sum_{i=1}^{n} (-1)^{i-1}\left(\frac{\tau_m}{\tau-\tau_m}\right)^i$$

$$+ \left(\frac{\exp(-\frac{t}{\tau})}{n}\right)\sum_{i=1}^{n} \frac{1}{\tau^i} \sum_{r=0}^{i-1} \frac{t^{i-r-1}}{(i-r-1)!}\tau^{r+1}\left(\left(-\frac{\tau_m}{\tau-\tau_m}\right)^{r+1} -1\right) \quad \ldots\ldots \quad (12)$$

Equation 12 can now be used to generate expressions for any desired value of the carbon number, n.

REFERENCES

1. Jenson, V. G., and Jeffreys, G. V., "Mathematical Methods in Chemical Engineering", Second Edition, Academic Press, 1977.
2. "CRC Handbook of Chemistry and Physics", R. C. Weast (ed.), 63rd edition, CRC Press Inc., Boca Raton, Florida, 1982.