APPENDIX 1

Scheme II - Middle Distillates Selectivity

The differential equations for this scheme can be written as follows

\[
\begin{align*}
\frac{dC_F}{dt} &= -k_1C_F - k_2C_F \\ 
\frac{dC_{MD}}{dt} &= k_1C_F - k_3C_{MD} \\ 
\frac{dC_{NG}}{dt} &= k_3C_{MD} + k_2C_F
\end{align*}
\]  
(A1.1) (A1.2) (A1.3)

Expressions were first derived considering that the concentration of middle distillates in the feedstock to be zero, i.e. feedstock is pure vacuum gas oil and does not contain any middle distillates. The mathematical expressions for the yield and maximum selectivity of middle distillates for this case can be derived using the boundary condition

When time \((t) = 0\), \(C_F = (C_F)_0\), \(C_{MD} = 0\) and \(C_{NG} = 0\)

By integration of equation (A 1.1) we can get the equation for the yield of feedstock

\[C_F = (C_F)_0 e^{-(k_1 + k_2)t} \]  
(A1.4)

On substitution of this expression in Equation (A1.2) and integration of resultant expression using the boundary conditions specified above will yield the expression for the yield of middle distillates as given below
\[ \frac{C_{MD}}{(C_F)_0} = \frac{k_1}{K-k_3} \left( e^{-k_3t} - e^{-kt} \right) \]  

(A1.5)

where \( K = k_1 + k_2 \).

The yield of naphtha and gas can be obtained by simple mass balance as follows:

\[ (C_F)_0 = C_F + C_{MD} + C_{NG} \]  

(A1.6)

\[ C_{NG} = (C_F)_0 - C_F - C_{MD} \]  

(A1.7)

By setting \( \frac{dC_{MD}}{dt} = 0 \), we can get the expression for the time at which maximum concentration of middle distillates fraction obtained. This is derived as follows:

\[ t_{\text{max}} = \frac{\ln \left( \frac{k_3}{k_1 + k_2} \right)}{k_3 - k_1 - k_2} \]  

(A1.8)

By substituting this equation for \( t_{\text{max}} \) in the expression for the yield of middle distillates will give the maximum yield of middle distillates obtained for a particular temperature for this case.

In another case, if feedstock contains some amount of middle distillates fraction, the initial concentration of middle distillates is not zero. The expressions for the product yields and the maximum concentration of middle distillates and the time at which this occurs can be derived as follows using the differential equations already presented above for this scheme

At time \( t=0 \), \( C_F = (C_F)_0 \), \( C_{MD} = (C_{MD})_0 \) and \( C_{NG} = 0 \).
From the integration of Equation (A1.1) and rearranging and substitution of the resultant expression in Equation (A1.2) will give the expression

\[
\frac{dC_{MD}}{dt} + k_3 C_{MD} = k_i (C_F)_0 e^{-(k_1 + k_2)t} \tag{A1.9}
\]

Integration of Equation (A1.9) and finding the value of integration constant using the boundary conditions will yield

\[
\frac{C_{MD}}{(C_F)_0} = \frac{(C_{MD})_0}{(C_F)_0} e^{-k_3 t} + \frac{k_i}{k_3 - K} \left( e^{-Kt} - e^{-k_3t} \right) \tag{A1.10}
\]

Where \( K = k_1 + k_2 \)

By setting \( \frac{dC_{MD}}{dt} = 0 \), we can get the expression for the time at which maximum concentration of the middle distillate fraction can be obtained. This is derived as follows:

\[
t_{\text{max}} = \frac{1}{K - k_3} \ln \left( \frac{K}{\alpha + \alpha (C_{MD})_0 (K - k_3)} \right) \tag{A1.11}
\]

Where \( \alpha = \frac{k_3}{k_1} \)

By substituting Equation (A1.11) in Equation (A1.10), will give the maximum yield of middle distillates obtained for a particular temperature for this case. The concentration of naphtha and gas can be obtained by mass balance.

\[
(C_F)_0 + (C_{MD})_0 = C_F + C_{MD} + C_{NG} \tag{A1.12}
\]

\[
C_{NG} = (C_F)_0 + (C_{MD})_0 - C_F - C_{MD} \tag{A1.13}
\]