Mathematical simulation of recycled flowsheets on the bases of lowtemperature methanol synthesis.

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Abstract.
Effective method for solution of recycled flowsheets mathematical models was suggested. For conventional recycled flowsheet an analytical solution was obtained. It was shown that purge flow depends on not only feed flow, but also on flows due to chemical conversion.

Earlier [1, 2] it was shown that methanol synthesis catalyzed by Cu-ZnO/Al2O3 proceeds the following two reaction routes:
\[
\begin{align*}
\text{CO}_2 + 3\text{H}_2 & = \text{CH}_3\text{OH} + \text{H}_2\text{O} + Q_1 & \text{K}_{p1} \\
\text{CO}_2 + \text{H}_2 & = \text{CO} + \text{H}_2\text{O} + Q_2 & \text{K}_{p2}
\end{align*}
\]

The simplest methanol synthesis flowsheet one can present as follows:

\[\text{M} \rightarrow \text{R} \rightarrow \text{Sep} \rightarrow \text{L} \rightarrow \text{gas}\]


If \(X_{ji}\) - molar flow of component \(i\) at flowsheet point \(j\) (\(j=1,...,8\), \(i=1,...,m\)), \(F_{1i}\) – feed molar flow of component \(i\), \(F_{3i}\) – molar flow of component \(i\) due to chemical reaction, \(X_j\) – total molar flow at point \(j\), \(S_{6i} = X_{6i}/X_{4i}\) - component \(i\) splitting coefficient at point 4 for point 6, \(S_7 = X_7/X_6\) – total splitting coefficient for point 7, then for points (1-8) we can write material balance:

1. \(X_{1i} = F_{1i}\)
2. \(X_{7i} - S_7 X_{6i} = 0\)
3. \(X_{2i} - X_{1i} - X_{7i} = 0\)
4. \(X_{3i} = F_{3i}\)
5. \(X_{4i} - X_{2i} - X_{3i} = 0\)
6. \(X_{6i} - S_{6i} X_{4i} = 0\)
7. \(X_{5i} - (1 - S_{6i}) X_{4i} = 0\)
8. \(X_{8i} - (1 - S_7) X_{6i} = 0\)

Solving the system of equations (1 – 8), we obtain \(X_{ji}\) (9-14) via \(F_{1i}, F_{3i}, S_{6i}, S_7\):

\[
X_{4i} = \frac{F_{1i} + F_{3i}}{1 - S_7 S_{6i}}
\] (9)
\[ X_{6i} = X_{4i} \cdot S_{6i} \]  
(10)

\[ X_{7i} = X_{4i} \cdot S_{7} \cdot S_{6i} \]  
(11)

\[ X_{2i} = F_{1i} + X_{7i} \]  
(12)

\[ X_{5i} = X_{4i} \cdot (1 - S_{6i}) \]  
(13)

\[ X_{8i} = X_{4i} \cdot S_{6i} \cdot (1 - S_{7}) \]  
(14)

\( S_{6i} \) is determined by solving separator equations. \( S_{7} \) is found from eq. (15) if recycle flow \( V_c \) is fixed:

\[ V_c - \frac{\sum_{i=1}^{m} (F_{1i} + F_{3i}) \cdot S_{7} \cdot S_{6i}}{1 - S_{7} \cdot S_{6i}} = 0 \]  
(15)

System (9 - 14) can be written in matrix form by analogy with [3]:

\[ S \cdot X = F \]  
(16)

Its solution is:

\[ X = S^{-1} \cdot F \]  
(17)

Here \( S \), \( S^{-1} \) - splitting coefficients matrices, \( X \) - vector - column of component molar flows, \( F \) - vector - column of feed molar flows.

Using molar flow 3 as a fictive feed is a development of work [3]. Analytical expressions similar to (9 - 14) for complex flowsheets become too large. To meet equation (15) a procedure is suggested:

1. From separator solution find \( S_{6i} \), new guess of \( S_{7} \) is taken from equation (15) solution.
2. \( X_{ji} \) are determined from eq. (16), which is solved \( m \) times.
3. If

\[ \frac{\sum_{i=1}^{m} X_{7i} - V_c}{V_c} \leq \varepsilon, \]  
(18)

then goto end of calculation, else set new \( S_{7} \) from eq.(15) and goto 2.

In given work molar flow \( F_{3i} \) are iterated until meeting inequality (18). It can be seen from (14,9) that the value of purge flow is determine by not only feed flows \( F_{1i} \), but also by molar flows due to chemical reaction. It means that even under stoichiometric mixture \( \text{CO}_2 + 3\text{H}_2\text{O} \) flowsheet feed a non-condensable \( \text{CO} \) will be accumulated in the system due to route (II). And than purge will be necessary.

Suggested method due to small number of iterations allows to use comprehensive reactor models in flowsheet. We used a model of reactor with Field’s tubes. Its mathematical model is given below:

\[ A \cdot N = A \cdot N_o \]  
(19)

\[ \frac{dN_1}{d\xi} = r_1 V_{cat} \]  
(20)

\[ \frac{dN_2}{d\xi} = r_2 V_{cat} \]  
(21)

\[ \frac{dT}{d\xi} = \frac{r_1 Q_1 + r_2 Q_2}{C_p} V_{cat} - K_s V_{cat} (T - T_x) \]  
(22)

\[ \frac{dT_x}{d\xi} = -K_s V_{cat} (T - T_x) \]  
(23)

Boundary conditions: \( \xi = 0 \Rightarrow T = T_s \), \( N_7 = N_{07} \), \( N_2 \)

\[ \xi = 1 \Rightarrow T_x = T_o \]
here \( A \) – atomic-molecular reaction matrix; \( \mathbf{N}_0, \mathbf{N} \) – vector-columns of inlet and current molar flows (\( \text{H}_2, \text{CO}, \text{CO}_2, \text{CH}_4, \text{N}_2, \text{H}_2\text{O}, \text{CH}_3\text{OH} \)); \( V_{\text{cat}} \) – total catalyst volume; \( \xi = \frac{V_{\text{cat}}}{V_{\text{cat}}} \); \( T, T_x \) – temperature in the catalyst layer and in annular space; \( r_1, r_2 \) – formation rate of \( \text{CH}_3\text{OH} \) and \( \text{CO} \) correspondingly, taken from [4]; \( K_t \) – total transfer coefficient; \( S \) – specific area of unit of catalyst volume.

Two models of the process in reactor were used for calculation:

1. Equilibrium route (II). Equation (21) was replaced by \( \ln K_{p2} = \ln N_2 + \ln N_6 - \ln N_1 - \ln N_3 \).

2. Both routes (I и II) are non-equilibrium, calculation by equations (19-23).

Figure in the text shows a comparison of calculated temperatures \( T \) and \( T_x \) by models 1 and 2.. It can be seen that there is remarkable difference between these two models in the beginning of catalyst layer, but outlet temperatures and productivity for the models differ slightly.

References.