

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

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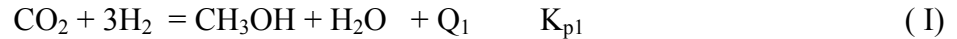
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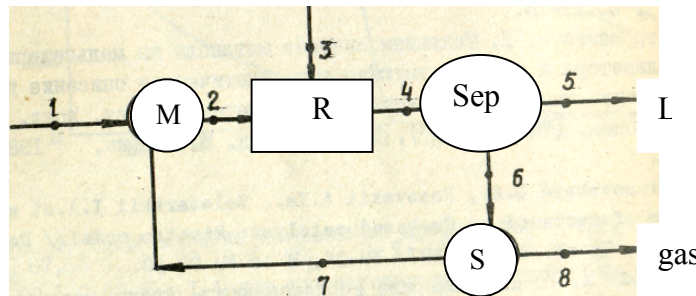
Abstract.

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 :



The simplest methanol synthesis flowsheet one can present as follows:



где M – mixer, R – reactor, Sep – separator, S – splitter, L – liquid products, gas – gas purge.

If X_{ji} - molar flow of component i at flowsheet point j ($j=1, \dots, 8$, $i=1, \dots, m$), 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:

$$X_{1i} = F_{1i} \quad (1)$$

$$X_{7i} - S_7 X_{6i} = 0 \quad (2)$$

$$X_{2i} - X_{1i} - X_{7i} = 0 \quad (3)$$

$$X_{3i} = F_{3i} \quad (4)$$

$$X_{4i} - X_{2i} - X_{3i} = 0 \quad (5)$$

$$X_{6i} - S_{6i} X_{4i} = 0 \quad (6)$$

$$X_{5i} - (1 - S_{6i}) X_{4i} = 0 \quad (7)$$

$$X_{8i} - (1 - S_7) X_{6i} = 0 \quad (8)$$

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

$$X_{4i} = \frac{F_{1i} + F_{3i}}{1 - S_7 S_{6i}} \quad (9)$$

$$X_{6i} = X_{4i} * S_{6i} \quad (10)$$

$$X_{7i} = X_{4i} * S_7 * S_{6i} \quad (11)$$

$$X_{2i} = F_{1i} + X_{7i} \quad (12)$$

$$X_{5i} = X_{4i} * (1 - S_{6i}) \quad (13)$$

$$X_{8i} = X_{4i} * S_{6i} * (1 - S_7) \quad (14)$$

S_{6i} is determined by solving separator equations. S_7 is found from eq. (15) if recycle flow V_c is fixed:

$$V_c - \sum_i^m \frac{(F_{1i} + F_{3i}) * S_7 * S_{6i}}{1 - S_7 * S_{6i}} = 0 \quad (15)$$

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

$$\mathbf{S} * \mathbf{X} = \mathbf{F} \quad (16)$$

Its solution is: $\mathbf{X} = \mathbf{S}^{-1} * \mathbf{F}$, (17)

Here \mathbf{S} , \mathbf{S}^{-1} - splitting coefficients matrices, \mathbf{X} - vector - column of component molar flows, \mathbf{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

$$\left| \frac{\sum_i^m X_{7i} - V_c}{V_c} \right| \leq \varepsilon, \quad (18)$$

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 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:

$$\mathbf{A} * \mathbf{N} = \mathbf{A} * \mathbf{N}_0 \quad (19)$$

$$\frac{dN_7}{d\xi} = r_1 V_{cat} \quad (20)$$

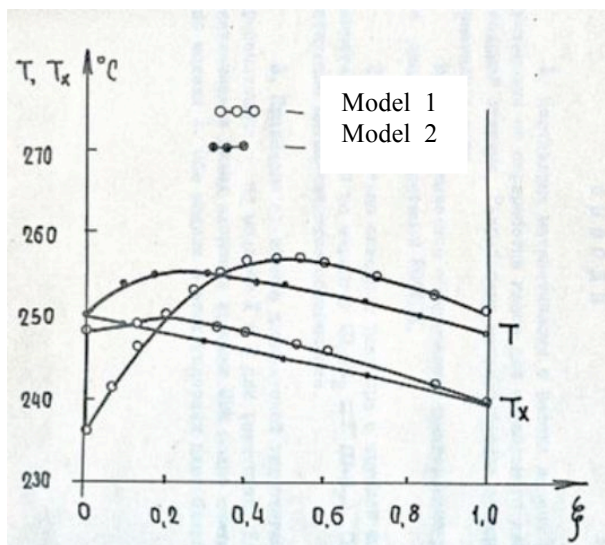
$$\frac{dN_2}{d\xi} = r_2 V_{cat} \quad (21)$$

$$\frac{dT}{d\xi} = \frac{r_1 Q_1 + r_2 Q_2}{C_p} V_{cat} - K_t S V_{cat} (T - T_x) \quad (22)$$

$$\frac{dT_x}{d\xi} = -K_t S V_{cat} (T - T_x) \quad (23)$$

Boundary conditions: $\xi = 0$ $T = T_s$, $N_7 = N_{07}$, N_2
 $\xi = 1$ $T_x = T_0$

here \mathbf{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_{cat} –total catalyst volume; $\xi = v_{\text{cat}}/V_{\text{cat}}$; T, T_x – temperature in the catalyst layer and in annular space; r_1, r_2 – formation rate of CH_3OH and 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 routs (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.

- 1).G.I. Lin, K.P. Kotyaev, A.Ya. Rozovskii, Stud.Surf.Sci.Catal., 130 (2000) 713.
- 2). A.Ya. Rozovskii, Yu.B. Kagan, G.I. Lin, Kinet. and Catal., 1976, v.17, №5, 1314-1320.
- 3). A.J. Weißenfelder, R.E. Olson. CEP, 1980, v.76, №1, p.40.
- 4). O.A. Malinovskaya, A.Ya. Rozovskii, I.A. Zolotarskii et.al., React. Kinet.Catal. Lett., 1987, v.34, №1, 87-92