

## ANALYSIS AND OPTIMIZATION OF REACTIVE DISTILLATION COLUMN

Ternovaya I.S., group 2KM61, the 1st of master course  
Scientific adviser Mityanina O.E., PhD, assistant,  
Linguistic supervisor Syskina A. A., Phd of Philology, associate professor  
Tomsk Polytechnic University  
Tomsk

Distillation is a common liquid-liquid separation process, applied in batch or continuous mode for binary or multi-component mixtures. Specialized reactors, such as reactive distillation columns, combine reaction and separation in a single unit. Nowadays, reactive distillation (RD) is paid much attention to industries. Due to its thermodynamic and economic advantages, RD can be considered as a successful example of the process intensification [1]. On the other hand, the combination of chemical reaction and separation in a single column reduces the number of valves available for control and causes high non-linearity, which can lead to steady-state multiplicities [2]. For example, output multiplicity, with multiple output values for the same input parameters, causes the column to drift to an undesirable steady-state [2].

The aim of the work is development of steady mathematical model and optimization of the process. A material balance of every component for each stage will be under steady state conditions if we express the liquid molar part:

$$\frac{1}{R+1} \left[ \frac{R}{R+1} \right]^0 \frac{1}{k_{0j}^0} + \frac{1}{R+1} \left[ \frac{R}{R+1} \right]^1 \frac{1}{k_{0j}^0 k_{1j}} + \frac{1}{R+1} \left[ \frac{R}{R+1} \right]^2 \frac{1}{k_{0j}^0 k_{1j} k_{2j}} + \dots + \left[ \frac{R}{R+1} \right]^i \frac{1}{\prod_{i=1}^M k_{ij}} = f_1^m(R), \quad (1)$$

where  $f_1^m(R)$  – function of material balance in the rectifying section.

$$\frac{1}{R+1} \left[ \frac{R}{R+1} \right]^0 \frac{1}{k_{0j}^0} + \frac{1}{R+1} \left[ \frac{R}{R+1} \right]^1 \frac{1}{k_{0j}^0 k_{ij}} + \frac{1}{R+1} \left[ \frac{R}{R+1} \right]^2 \frac{1}{k_{0j}^0 k_{1j} k_{2j}} + \dots + \left[ \frac{R}{R+1} \right]^i \frac{1}{\prod_{i=1}^M k_{ij}} + \frac{U_i}{L_i} \sum_{\rho=1}^m v_{j,\rho} r_{i,\rho} - \frac{x_{ij}}{x_{0j}} = f_2^m(R), \quad (2)$$

where  $f_2^m(R)$  – function of material balance in the reactive section

$$\frac{1}{P+1} \left[ \frac{P}{P+1} \right]^0 k_{0j}^0 + \frac{1}{P+1} \left[ \frac{P}{P+1} \right]^1 k_{0j}^0 k_{1j} + \frac{1}{P+1} \left[ \frac{P}{P+1} \right]^2 k_{0j}^0 k_{1j} k_{2j} + \dots + \left[ \frac{P}{P+1} \right]^i \prod_{i=1}^{N+1} k_{ij} - \frac{x_{ij}}{x_{0j}} \equiv f_3^m(P), \quad (3)$$

where  $f_3^m(P)$  – function of material balance in the stripping section.

The heat balance is considered under the steady state conditions likewise the mass balance:

$$\frac{DH}{G} + \frac{L_0}{G} \left( \frac{DH_{L_0}}{G} + \frac{L_0^{i-1} DH_{L_0} + L_0^i (H_{L_0} - r_0) + \dots + L_0^{i-1} (Q_c - r_{i-1} G)}{G^i} + \frac{(Q_c - r_i G)}{G} \right) + \frac{Q_c}{G} - H_{G_{i+1}} \equiv f_1^h(R), \quad (4)$$

where  $f_1^h(R)$  – function of heat balance in the rectifying section.

$$\frac{DH_{L_0}}{G} + \frac{L_0}{G} \left( \frac{DH_{L_0}}{G} + \frac{L_0^{i-1}DH_{L_0} + L_0^i(H_{L_0} - r_0) + \dots + L_0^{i-1}(Q_c - r_{i-1}G)}{G^i} + \frac{(Q_c - r_iG)}{G} \right) - H_{G_{i+1}} -$$

$$U_i \sum_{\rho=1} v_{j,\rho} r_{i,\rho} \cdot \Delta H_{ch.r.} + \frac{Q_c}{G} \equiv f_2^h(R), \quad (5)$$

where  $f_2^h(R)$  – function of heat balance in the stripping section.

$$\frac{WH_{L_0}}{L} + \frac{G_0}{L} \left( \frac{WH_{L_0}}{L} + \frac{G_0^{i-1}WH_{G_0} + G_0^i(H_{L_0} - r_0) + \dots + G_0^{i-1}(r_{i-1}L - Q_b)}{L^i} + \frac{(r_iL - Q_b)}{L} \right) -$$

$$H_{L_{i+1}} + \frac{Q_b}{L} \equiv f_3^h(P), \quad (6)$$

where  $f_3^h(P)$  – function of heat balance in the reactive section.

Steady state multiplicity analysis must reveal sources of nonlinearity. As seen in the mathematical model, control parameters and nonlinear terms are the vapor and reflux ratios. Every solution of the equations (1), (2), (3), (4), (5), (6) with physical meanings of R, which satisfy the following conditions (7) corresponds to a unique steady state.

$$f_1^m(R) = 0, f_2^m(R) = 0, f_1^h(R) = 0, f_2^h(R) = 0, f_3^m(P) = 0, f_3^h(P) = 0 \quad (7)$$

Hence, any argument with physical meaning, satisfying the equalities constitutes a point of multiplicity:

$$\frac{\partial f_1^m}{\partial R} = 0, \frac{\partial f_2^m}{\partial R} = 0, \frac{\partial f_1^h}{\partial R} = 0, \frac{\partial f_2^h}{\partial R} = 0, \frac{\partial f_3^m}{\partial P} = 0, \frac{\partial f_3^h}{\partial P} = 0. \quad (8)$$

Initial conditions:

$$R=0, U_i = 0, x_{ij} = x_j, H_{G_{i+1}} = r_0, \quad (9)$$

$$P=0, U_i = 0, x_{ij} = x_0, H_{L_{i+1}} = H_{L_0}. \quad (10)$$

The result of the calculations is presented in table 1.

Table 1. Reflux (R) and vapor (P) ratio, corresponding to steady states multiplicity region.

Rectifying and reactive sections		Stripping section	
№ of tray	R	№ of tray	P
0 (condenser)	-	11	-
1	0.01	12	-
2	0.07	13	-
3	2.36	14	1.11;0.07
4	-	15	0.79,0.57
5	0.42	16 (reboiler)	-
6	1.46		
7	2.49		
8	3.47		
9	4.48		
10 (feed tray)	-		

Table 1 shows that the vapor and reflux ratios, corresponding to one steady state, should meet the following requirements:  $R \geq 4.48$ ,  $P \geq 1.11$ . Otherwise, there is a risk to operate the column in multiplicity region.

With using physical meaning of reflux ratio  $R=L_0/D$ , material balance of the reactive section is considered as functions of substance consumption and supply

$$\begin{cases} F^{supply} = \frac{L_d}{R} + \frac{L_d}{R} \cdot \frac{L_d}{k_i} + \left[ \frac{L_d}{R} \right] \cdot \frac{L_d^2}{k_i \cdot k_{i-1}} + \dots + \frac{L_d^i}{\prod_{i=1}^M k_i} + k_f \frac{x^{i-but} \cdot \gamma^{i-but}}{x^{MeOH} \cdot \gamma^{MeOH}} \\ F^{consumption} = L_d \frac{x_i}{x_d} + k_f \frac{x^{MTBE} \cdot \gamma^{MTBE}}{K_{eq}(x^{MeOH} \cdot \gamma^{MeOH})^2}, i = 1, 2 \dots s \end{cases} \quad (12)$$

$L_d$  – distillate flow rate, mole/s;  $s$  – number of stages in reactive section;  $k_i$  – vaporliquid equilibrium constant;  $k_f$  – forward reaction rate constant;  $K_{eq}$  – equilibrium constant;  $R$  – molar reflux ratio;  $\gamma$  – activity coefficient;  $x$  – liquid molar part; superscripts  $i$ -but, MeOH, MTBE correspond to isobutylene, methanol and MTBE respectively.

Figures 1 and 2 show relationships between functions  $F_{supply}$ ,  $F_{consumption}$  and component concentration.

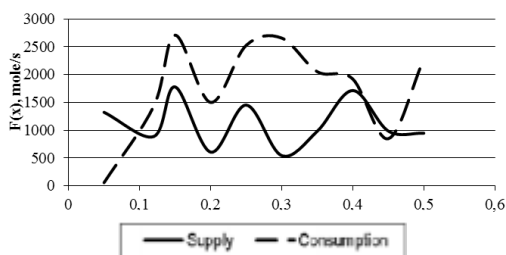


Figure 1. Interrelation between functions  $F_{supply}$ ,  $F_{consumption}$  and methanol concentration

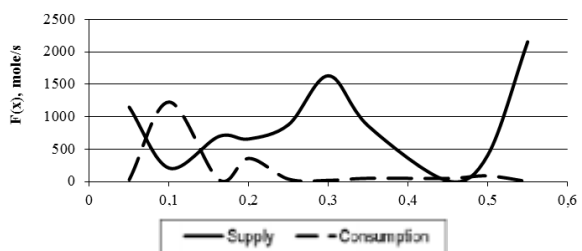


Figure 2. Interrelation between functions  $F_{supply}$ ,  $F_{consumption}$  and MTBE concentration

According to fig. 1-2, the points of intersection of supply and consumption lines are related to output steady states of reactive section of the column. Steady state compositions are presented in Table 2.

Table 2. Compositions of possible steady states.

	$C_1$	$C_2$	$C_3$
$x^{i-bu}$	0.08	0.08	0.01
$x^{MeOH}$	0.41	0.47	0.11
$x^{MTBE}$	0.14	0.08	0.47
$x^{i-but}$	0.37	0.37	0.41
S,%	28.9	16.5	97.0

Table 2 illustrates that the most desirable steady state is  $C_3$ , which corresponds to the best product yield (X).

The method of steady state multiplicity analysis enables to:

- 1) reveal different multiplicities regions without modification of the model;
- 2) decrease simulation time and avoid non-optimal solutions;
- 3) research system behavior under the condition of different disturbances;
- 4) recommend control parameters intervals corresponding to one steady state region;
- 5) reveal all possible steady states;

6) determine stability of the steady states.

In the future it planned to check the adequacy of the obtained model through the substitution of data from the company «Omsky kauchuk».

**References:**

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