Petroleum and Coal

MATHEMATICAL MODELING AND STEADY STATES MULTIPLICITY ANALYSIS OF METHYL *tert*-BUTYL ETHER REACTIVE DISTILLATION SYNTHESIS

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Abstract

The paper is devoted to a new approach to steady state multiplicity analysis of methyl *tert*-butyl ether (MTBE) production by means of reactive distillation. Reactive distillation systems are characterized by input and output multiplicities, which may cause complex and unpredictable behavior of the process. The fundamental mathematical model, which enables to reveal potential sources of nonlinearity of the process, is proposed. As the result of input multiplicity analysis, intervals of one steady state were found for vapor and reflux ratio. Output multiplicity analysis showed three possible steady states in the reactive section of the column, one of which is corresponded to the maximal product yield. The advantage of the method is the ability to find "input-output" multiplicities on every stage of the column by using control parameters of the feed, reboiler and condenser only.

Keywords: reactive distillation; MTBE; mathematical modeling; stability analysis; steady state multiplicity.

1. Introduction

Reactive distillation is considered as a promising and economically sound way of the process realization in comparison with the conventional schemes, where separation unit follows reactive apparatus. The reactive distillation is successfully implemented in a wide range of important chemical processes, for instance, cryogenic air separation [1] syntheses, biodiesel production [2], synthesis of petrol additives, such as ethyl *tert*-butyl ether (ETBE), methyl *tert*-butyl ether (MTBE) [3-4].

Nowadays a large number of scientific works devoted to design, optimization and dynamical analysis of etherification processes in reactive distillation column [5-7], such as Singh [5], Chen *et al.* [6], Singh [7] *etc.* was published, where the presence of steady states multiplicity with different outputs of desired product was mentioned. Such processes require an effective control based on mathematical models, embedded in control algorithm.

Generally, steady states multiplicity is caused by complexity of the combination of chemical reaction and separation in a one column which reduces the number of valves available for control and causes high non-linearity, which can lead to steady-state multiplicities [8]. But in case of reactive distillation etherification processes nonlinearity of material, energy and heat balance (MEH) equations is the result of nonideality of vapor-liquid equilibrium (VLE) and kinetic features. Since these reveal high nonideality of the behavior, the reaction rates are defined by activities of the components [9].

There are many approaches to proper design of reactive distillation columns. For example, Huang and Nakaiwa [4] suggested a sequential procedure to determine an appropriate process configuration for internal heat integration within reactive distillation column. The method shows high effectiveness, but restricted by thermodynamic properties of reacting mixtures and does not reveal all the possible steady states. One of the last suggested approaches to reactive distillation design is discussed by Mansouri *at al.* [10]. The method based on the element concept, which is used to translate a system of compounds into elements, is proposed

to MTBE synthesis. Visualization makes the method useful, but it cannot be implemented for multicomponent systems and does not consider inert components in the mixture.

There are several mathematical models and formulations of reactive distillation processes, however some of them are very complex and require special software for calculations, for example, some researches consider the design of reactive distillation columns in terms of a mixed-integer nonlinear programming (MINLP) [11]. The potential problems of the approach are difficulties in searching of global optimum and complexity of calculations. In general, formulation of the design of reactive distillation columns as an optimization problem [12] takes into consideration thermodynamic and kinetic restrictions and offers a plenty of possible variants of the process implementation, but does not show regions of potential multiplicity and undesirable work of the column. Some models contain plenty of assumptions or developed based on empirical correlations [13-14].

The authors of the work aimed to consider one of the most researched and discussed reactive distillation processes – synthesis of MTBE, to create a mathematical model, which would be suitable for the precise process control, prediction of the synthesis behavior and stability analysis and to find "input-output" multiplicities on every stage of the column by using control parameters of the feed, reboiler and condenser only.

2. Experimental

The authors in their work implemented method of mathematical modeling. The models used are built on fundamental principles of reactive distillation process. Verification of the models is based on published experimental data given in works of Hauan, Hertzberg and Lien [15]. Software used: MathCad 14, Hyprotech HYSYS 2006, Pro II, Microsoft Excel 2003.

2.1. Design of mathematical model

Assumptions

We considered a reactive distillation column of MTBE synthesis with a partial condenser. The rectifying section consists of M stages, the stripping section consists of N+1 stages and a feed tray. The numbering of the stages in the rectifying section stages runs from 0 (for a condenser) to M, in the stripping section – from 0 to N+1 (the last tray of this section is the feed tray). The feed is in the vapor (isobutylene, n-butene) and the liquid phase (methanol). The liquid and the vapor leaving each stage are under equilibrium conditions. Fig.1 shows the simplified scheme of the column.
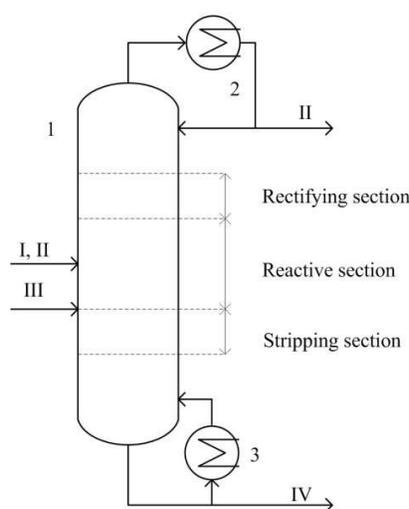

Fig. 1. Scheme of the reactive distillation column of methyl *tert*-butyl ether synthesis. I, II, III, IV – streams of isobutylene, n-butene, methanol and MTBE respectively; 1– reactive distillation column; 2 – condenser; 3 – reboiler.

The chemical reaction of MTBE synthesis can be described by the following scheme:

$$CH_3OH + CH_2=C(CH_3)_2 \leftrightarrow CH_3\text{-}O\text{-}C(CH_3)_3 + \Delta H_{ch.r} \tag{1}$$

The reactive zone of the column is located under the feed tray; hence, we can consider the reactive zone as a part of the rectification zone.

Material balance

The basic equation for vapor-liquid equilibrium calculations:

$$y_{ij} = \gamma_{ij} k'_{ij} x_{ij} \tag{2}$$

A material balance of every component for each stage under steady state conditions will be if we express the liquid molar part:

Stage №0 (condenser):

$$x_{1j} = \frac{D}{G} x_{0j} + \frac{L_0}{G \cdot k_{1j}} x_{0j} \tag{3}$$

Stage №1:

$$Gy_{2j} + L_0 x_{0j} = Gy_{1j} + Lx_{1j} \tag{4}$$

or (using ex. (3) for x_1):

$$x_{2j} = \frac{D}{G} x_{0j} + \frac{L}{G \cdot k_{2j}} x_{1j} = \frac{D}{G} x_{0j} + \left[\frac{D}{G}\right] \cdot \frac{L_0}{G \cdot k_{2j}} \cdot x_0 + \frac{L_0^2}{G \cdot k_{1j} \cdot k_{2j}} \cdot x_{0j} \tag{5}$$

Stage № i:

$$x_{ij} = \left[\frac{D}{G}\right] \frac{L_0^0}{G^0 k_{0j}^0} x_{0j} + \left[\frac{D}{G}\right] \frac{L_0^1}{G^1 k_{0j}^0 k_{1j}} x_{0j} + \left[\frac{D}{G}\right] \frac{L_0^2}{G^2 k_{2j} k_{1j} k_{0j}^0} x_{0j} + \ldots + \frac{L_0^i}{G^i \prod\limits_{i=1}^{M} k_{ij}} x_{0j} \tag{6}$$

Thereby, for each component in the liquid phase on the stage number i (steady state conditions):

$$\frac{1}{R+1}\left[\frac{R}{R+1}\right]^0 \frac{1}{k_{0j}^0} + \frac{1}{R+1}\left[\frac{R}{R+1}\right]^1 \frac{1}{k_{0j}^0 k_{1j}} + \frac{1}{R+1}\left[\frac{R}{R+1}\right]^2 \frac{1}{k_{2j} k_{1j} k_{0j}^0} + \ldots + \left[\frac{R}{R+1}\right]^i \frac{1}{\prod\limits_{i=1}^{M} k_{ij}} - \frac{x_{ij}}{x_{0j}} \equiv f_1^m(R) \quad (7)$$

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

The vapor stream on each stage is defined after considering the stripping section. In the reactive zone of the column, kinetics is expressed as:

$$U_i \sum_{\rho=1}^{m} v_{j,\rho} r_{i,\rho} \tag{8}$$

Hence, the material balance of the component, participating in the chemical reactions can be written as following:

$$\frac{1}{R+1}\left[\frac{R}{R+1}\right]^0 \frac{1}{k_{0j}^0} + \frac{1}{R+1}\left[\frac{R}{R+1}\right]^1 \frac{1}{k_{0j}^0 k_{1j}} + \frac{1}{R+1}\left[\frac{R}{R+1}\right]^2 \frac{1}{k_{2j} k_{1j} k_{0j}^0} + \ldots + \left[\frac{R}{R+1}\right]^i \frac{1}{\prod\limits_{i=1}^{M} k_{ij}} +$$

$$+ \frac{U_i}{L_i} \sum_{\rho=1}^{m} v_{j,\rho} r_{i,\rho} - \frac{x_{ij}}{x_{0j}} \equiv f_2^m(R) \tag{9}$$

here $f_2^m(R)$ - function of material balance in the reactive section.

Using the same approach we can find the material balance for the stripping section on the column.

For the stripping section, the material balance is found as following:

$$\frac{1}{P+1}\left[\frac{P}{P+1}\right]^0 k_{0j}^0 + \frac{1}{P+1}\left[\frac{P}{P+1}\right]^1 k_{0j}^0 k_{1j} + \frac{1}{P+1}\left[\frac{P}{P+1}\right]^2 k_{2j}k_{1j}k_{0j}^0 + ... + \left[\frac{P}{P+1}\right]^i \prod_{i=1}^{N+1} k_{ij} - \frac{x_{ij}}{x_{0j}^`} \equiv f_3^m(P) \quad (10)$$

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

Equations (7), (9), (10) show, that potential sources of nonlinearity are kinetics (due to nonlinear dependencies of activity coefficients and kinetic constant from temperature) and nonlinear members of the equations, corresponding to the mass-exchange on the stages.

Heat balance

The heat balance is considered under the steady state conditions likewise the mass balance. The model for the stripping zone is given below.

Stage №0 (condenser):

$$GH_{G_1} = DH_{L_0} + LH_{L_0} + Q_c \quad (11)$$

Stage №1:

$$GH_{G_1} + LH_{L_0} = GH_{G_1} + LH_{L_0} \quad (12)$$

Stage № i (if we express liquid enthalpy for the stage number i+1):

$$H_{G_{i+1}} = \frac{DH_{L_0}}{G} + \frac{LH_{L_i}}{G} + \frac{Q_c}{G} \quad (13)$$

Sequentially expressing liquid enthalpy on each stage through enthalpy of the residue, we can write:

$$\frac{DH_{L_0}}{G} + \frac{L_0}{G}\cdot\left(\frac{DH_{L_0}}{G} + \frac{L_0^{i-1}DH_{L_0} + L_0^i\cdot\left(H_{L_0} - r_0\right) + ... + L_0^{i-1}\cdot\left(Q_c - r_{i-1}G\right)}{G^i} + \frac{\left(Q_c - r_iG\right)}{G}\right) + \frac{Q_c}{G} - H_{G_{i+1}} \equiv f_1^h(R) \quad (14)$$

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

There is extra heat in reactive section due to the chemical reaction (1). As far as the chemical reaction has an exothermic effect, heat balance of the reactive zone can be written as

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

$$-H_{G_{i+1}} - U_i\sum_{\rho=1}^{m} v_{j,\rho} r_{i,\rho}\cdot\Delta H_{ch.r.} + \frac{Q_c}{G} \equiv f_2^h(R) \quad (15)$$

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

Using the approach, expressed in (11) - (14) to the heat balance, we can express enthalpy of the liquid on each stage in the stripping section

$$\frac{WH_{L_0'}}{L} + \frac{G_0'}{L}\cdot\left(\frac{WH_{L_0'}}{L} + \frac{G_0'^{i-1}WH_{G_0'} + G_0'^i\cdot\left(H_{L_0} + r_0'\right) + ... + G_0'^{i-1}\cdot\left(r_{i-1}'\cdot L - Q_b\right)}{L^i} + \frac{\left(r_iL - Q_b\right)}{L}\right) + \frac{Q_b}{L} - H_{L_{i+1}} \equiv f_3^h(P) \quad (16)$$

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

Dependencies (14), (15), (16) for the stripping, rectification and reactive zones respectively can be used for research of the influence of the reboiler and condenser duties on the bottom and distillate compositions and stream rates.

Detailed vapor-liquid equilibrium analysis of the system is considered by authors in previous publications [16].

2.2. Model verification

Verification of the model is presented on fig. 2. The calculation results were compared to Hauan [15].
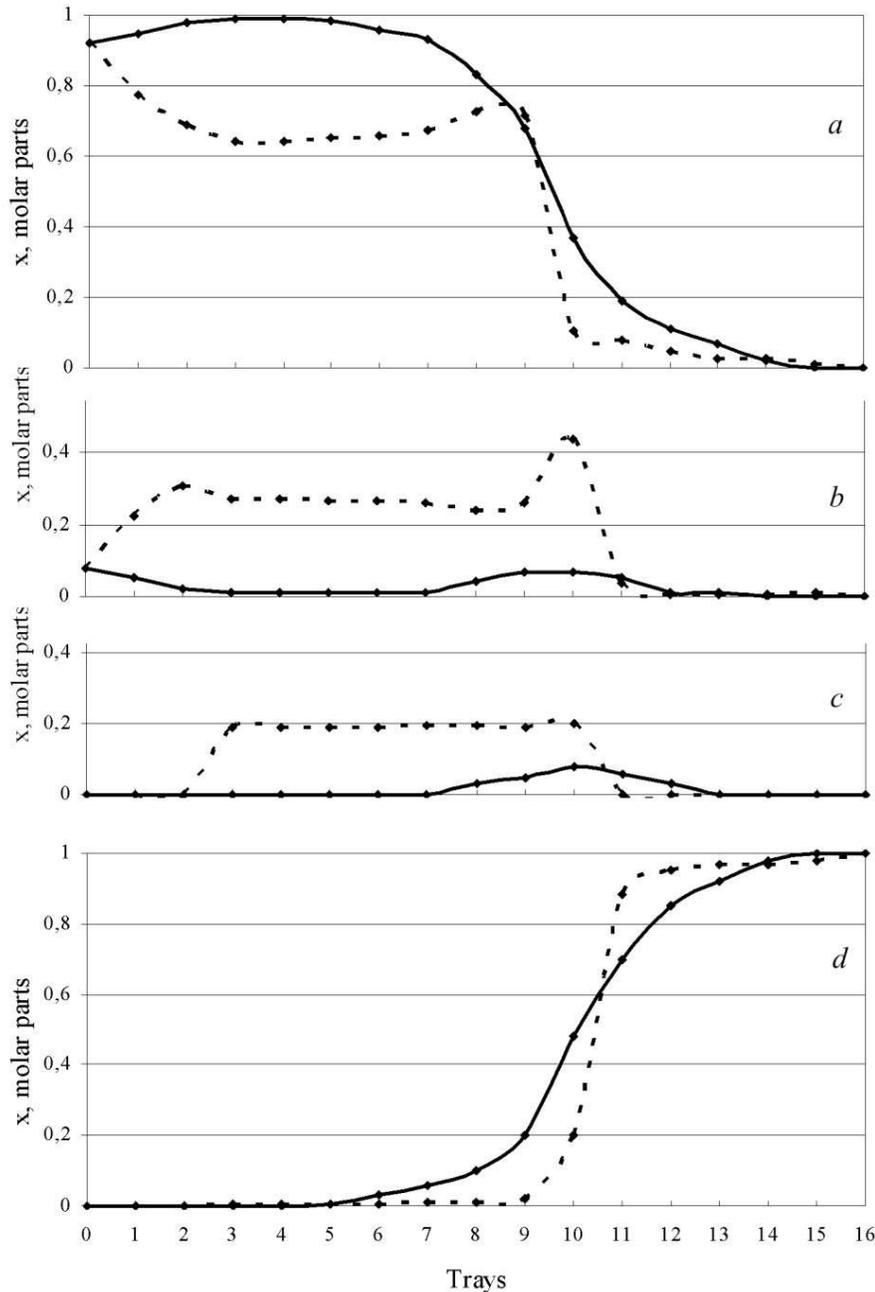
Fig. 2. Result of the concentration calculation: a) n-buten; b) methanol; c) isobutylene; d) MTBE.
Dashed line – data from Hauan [15]; fully-drawn line – calculations.

The fig. 2 shows that the concentrations of every component in the distillate and bottom streams are in a good accordance with the data of Hauan [15].

3. Results and discussion

Reactive distillation columns are characterized by control difficulties caused by steady states input and output multiplicities. Input multiplicity, with the same output values yielded for different inputs and output multiplicity, with multiple output values for the same input parameters, cause the column to drift to an undesirable steady-state and "wrong" control actions [8].

Modern methods of multiplicity analysis are based on mathematical models of the process. The model, proposed by the authors in the previous chapters for all sections of the column, is based on fundamental principles of the process and can be used for investigation of the main control parameters influence on the system, multiplicity and stability analysis.

3.1. Input multiplicity

In order to implement steady state multiplicity analysis, one should reveal sources of potential nonlinearity. As provided by the mathematical model of the process, control parameters and nonlinear members of the model are the vapor and reflux ratio. Every solution of the equations (7), (9), (10), (14), (15), (16) with physical meanings of R, P which satisfy the following conditions

$$f_1^m(R)=0, f_2^m(R)=0, f_1^h(R)=0, f_2^h(R)=0 \quad , \tag{17}$$

$$f_3^m(P)=0, f_3^h(P)=0 \quad , \tag{18}$$

corresponds to the unique steady state. Hence, any argument with physical meaning, which corresponds to equalities

$$\frac{\partial f_1^m}{\partial R}=0, \frac{\partial f_2^m}{\partial R}=0, \frac{\partial f_1^h}{\partial R}=0, \frac{\partial f_2^h}{\partial R}=0 \quad , \tag{19}$$

$$\frac{\partial f_3^m}{\partial P}=0, \frac{\partial f_3^h}{\partial P}=0 \quad , \tag{20}$$

is the point of multiplicity region [17].

Initial conditions: $R=0, U_i=0, x_{ij}=x_{0j}$; $\qquad H_{G_{i+1}}=H_{L_0}-r_0$;

$P=0, U_i=0, x_{ij}=\grave{x}_0$, $H_{L_{i+1}}=H_{L_0}$.

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 show that the vapor and reflux ratios, corresponding to one steady state, should meet the following requirements: R≥4.48, P≥1.11. Otherwise, there is the risk to operate the column in multiplicity region.

3.2 Output multiplicity

For the output multiplicity analysis of the process the reactive section of the column is considered, due to complexity of separation and reaction combination. In this case, it is advisable to rewrite material balance equation of the reactive section (9) as functions of subs-

tance consumption and supply with the assumption of liquid holdup (U) and catalyst weight (M_c) to be constant.

Kinetic equation for MTBE synthesis is expressed as [5]

$$r = M_c k_f \left(\frac{x_{IB} \cdot \gamma_{IB}}{x_{MeOH} \cdot \gamma_{MeOH}} - \frac{x_{MTBE} \cdot \gamma_{MTBE}}{K_{eq} \left(x_{MeOH} \cdot \gamma_{MeOH} \right)^2} \right), \tag{21}$$

superscripts IB, NB, MeOH, MTBE correspond to isobutylene, n-butene, methanol and MTBE respectively.

With using physical meaning of reflux ratio $R = L_0 / D$, material balance of the reactive section is considered as following system:

$$\begin{cases} F^{sup\,ply} = \dfrac{L_0}{R} + \dfrac{L_0}{R} \cdot \dfrac{L_0}{k_i} + \left[\dfrac{L_0}{R} \right] \cdot \dfrac{L_0^2}{k_i \cdot k_{i-1}} + \ldots + \dfrac{L_0^i}{\prod\limits_{i=1}^{M} k_i} + k_f \dfrac{x^{i-but} \cdot \gamma^{i-but}}{x^{MeOH} \cdot \gamma^{MeOH}} \\[4ex] F^{consumption} = L_0 \dfrac{x_i}{x_0} + k_f \dfrac{x^{MTBE} \cdot \gamma^{MTBE}}{K_{eq} \left(x^{MeOH} \cdot \gamma^{MeOH} \right)^2} \end{cases} \quad , \ i=1,2\ldots s \tag{22}$$

Index of the component j is omitted for the simplicity.

Figures 3, 4 show relationships between functions F^{supply}, $F^{consumption}$ and component concentration.
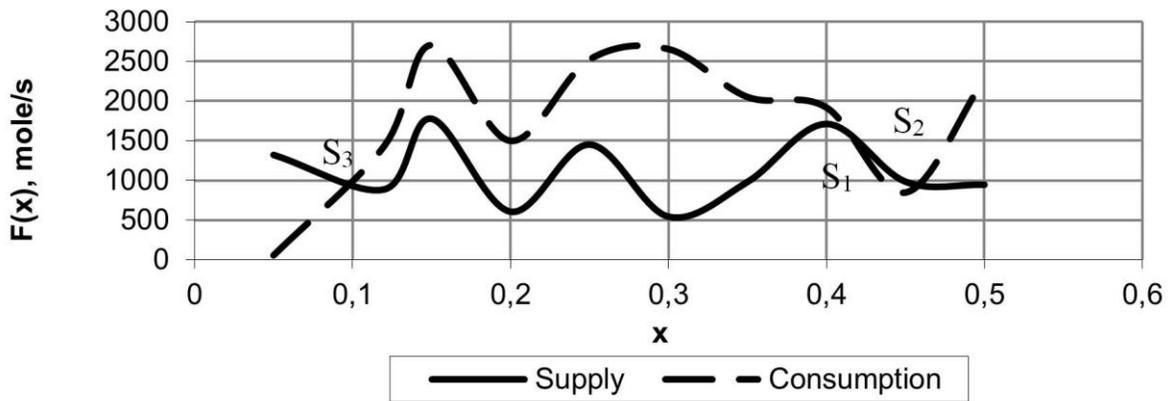

Fig. 3. Dependence of F^{supply} and $F^{consumption}$ from methanol concentration in reactive section of the column
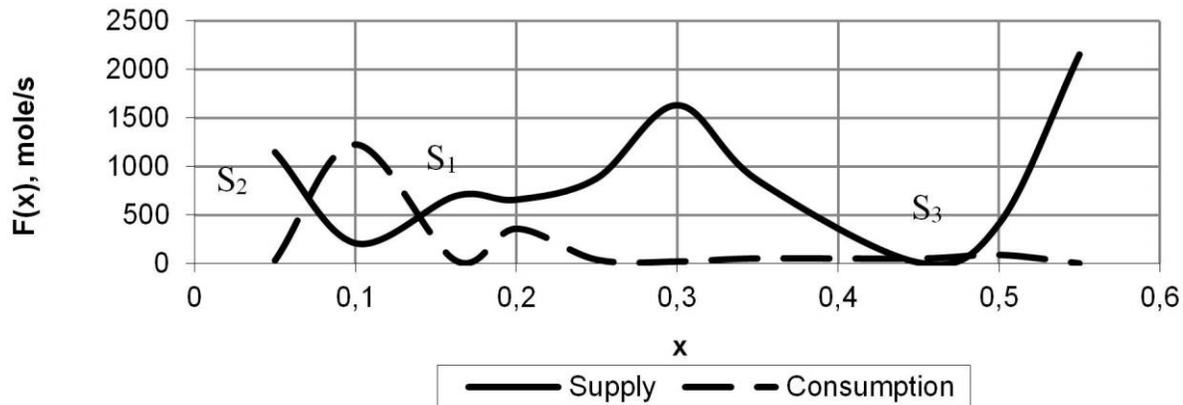

Fig. 4. Dependence of F^{supply} and $F^{consumption}$ from MTBE concentration in reactive section of the column

According to fig. 3-4, the points of intersection of supply and consumption lines are related to output steady states of reactive section of the column. Steady states compositions are presented in Table 2.

Table 2. Material flows compositions of output steady states in reactive section

S₁		S₂		S₃	
x_{IB}	0.08	x_{IB}	0.08	x_{IB}	0.01
x_{MeOH}	0.41	x_{MeOH}	0.47	x_{MeOH}	0.11
x_{MTBE}	0.14	x_{MTBE}	0.08	x_{MTBE}	0.47
x_{NB}	0.37	x_{NB}	0.37	x_{NB}	0.41
X, %	28.9	X, %	16.5	X, %	97.0

Here Table 2 illustrates that the most desirable steady state is S_3, which corresponds to the best product yield.

4. Conclusion

The new approach to forming of reactive distillation mathematical model is offered. The obtained model is relatively simple and can be used for stability analysis without any special software. On the other hand, this model is based on fundamental principles of the process and can be applied for control algorithm and also for research, designing and stability analysis.

The main feature of the approach is the ability to find "input-output" multiplicities on every stage of the column by using parameters of the feed, reboiler and condenser duties. The calculation results are satisfactory close to the data obtained by other researchers.

The method of steady state multiplicity analysis enables to:
- reveal different multiplicities regions without model modification;
- decrease the designing time and avoid non-optimal solutions;
- investigate system behavior under the condition of different disturbances;
- recommend control parameters intervals corresponding to unique steady state region.

Symbols

D	distillate rate, mole/s	k_f	forward reaction rate constant, mole/s
$\Delta H_{ch.r}$	specific chemical reaction heat effect, J/mole	k'	equilibrium constant of an ideal mixture
H	enthalpy, J/mole	r	specific evaporation heat, J/mole
G	vapor rate, mole/s	r'	specific evaporation heat of the residue, J/mole
G'	vapor stream from the reboiler, mole/s	X	product yield, %
L	reflux rate, mole/s	x	liquid molar part
L'	residue, mole/s	x'_0	molar part of the component in the reboiler
M	number of stages in rectifying section	P	molar vapor ratio
M_c	catalyst weight, kg	y	vapor molar part
N	number of stages in stripping section	i	stage number
Q_c	condenser duty, J/s	j	component number
Q_b	reboiler duty, J/s	γ	activity coefficient
R	molar reflux ratio	ρ	number of specific chemical reaction
P	molar vapor ratio	v	stoichiometric coefficient
K_{eq}	kinetic equilibrium constant	r	specific chemical reaction
k	equilibrium constant	U	liquid holdup, mole

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