SIMULATION OF INDUSTRIAL MTBE PRODUCTION IN REACTIVE DISTILLATION COLUMN USING ASPEN HYSYS

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Abstract

Simulation of reactive distillation by using special engineering software is promising way to its design, research and optimization. In this work we considered the industrial-scale facility of Western Siberia, which includes a line of methyl tert-butyl ether production in a reactive distillation unit. Aspen HYSYS® was used as an instrument of simulation and further optimization studies. The calculation error of the model does not exceed 5%. Simulation of the feedstock composition changes showed that more preferable hydrocarbon fraction for the process is isobutene-isobutylene fraction. After the optimization study we obtained values of optimal reflux ratio for isobutene-isobutylene fraction to be 0.75 and for butylene-isobutylene fraction – 0.80; optimal methanol flowrate for isobutene-isobutylene fraction is 6.500 ton/h, for butylene-isobutylene fraction –6.000 ton/h.

Keywords: : reactive distillation; MTBE; simulation; industrial process; Aspen HYSYS®.

1. Introduction

Oxygenated additives are widely used in gasoline blending as alternative to tetra ethyl lead and aromatics. These additives improve the octane and combustion quality of gasoline and reduce greenhouse gas emissions [1]. The most popular oxygenated chemicals for liquid fuels are methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), methyl tert-amyl ether (TAME).

Operating experience of lab-scale and industry-scale MTBE production showed that maximum output of MTBE can be achieved using reactive distillation (RD) process, which is combination of chemical reaction and separation in one unit [2-4].

Despite all economic advantages of the process, [5-6] for most liquid-phase reversible reactions, design, simulation and control of RD are complicated due to interaction between chemical reaction and separation [7], heat integration [8-9], azeotropic mixtures [10]. In addition, many researchers draw attention to input and output multiplicities during production of MTBE in RD columns [11-14]. Experimental studies of proper column confi-guration and optimal operating conditions are expensive and sometimes infeasible within the conditions of industrial process. Therefore, mathematical simulation and developing a reliable model of the MTBE reactive distillation is an issue of current scientific interest.

There are many approaches to modeling and pre-analysis of reactive distillation, such as disjunctive programming [15], mixed integer nonlinear programming (MINLP) [16], graphical method [17], methods, based on wave propagation theory [18], stochastic methods [19-20]. Nowadays, design, optimization and research of many popular chemical engineering processes, including RD, can be implemented by means of special software. Most simulation studies and further analyses of RD etherification processes are conducted using engineering software like Aspen HYSYS®, Simulink etc.

A lot of recent research papers are devoted to simulation of RD problems by means of Aspen HYSYS® [11, 21-23], some of them consider MTBE production [11-12] but mostly on a pilot or laboratory scale.

In this work we aimed to develop a steady state model of industrial-scale MTBE synthesis implemented in production on one of the largest oil refineries of Western Siberia. The model became a basis for control parameter study and research of the influence of hydrocarbon feedstock on product yield.

2.Experimental

We implemented mathematical modeling as the main method. All the models used are based on physical and chemical fundamentals of reactive distillation. To verify the model we compared the calculation results with the data of industrial facility provided for January 2016. Software used: Aspen HYSYS® v.7.3, Microsoft Excel 2010.

2.1 Initial data

The subject of research is industrial plant of RD MTBE production within the large-scale refinery of Russia located at Western Siberia. The plant capacity is 239,000 tons of MTBE per year. The facility under consideration consists of two parallel production lines including removal of nitrogen-containing impurities from feedstock, MTBE production, methanol removal from waste fraction and two units of methanol and nitrogen-containing compounds separation from flush water.

MTBE is produced by reactive distillation from methanol and isobutylene over ion-exchange catalyst with further separation of the end-products.

Mechanism of MTBE synthesis

The mechanism of MTBE synthesis reaction (1) involves formation of carbonium cations with heat releasing at the rate of 66 kJ/mole.

$$H_3C-\underset{\underset{CH_3}{|}}{C}=CH_2 \; + \; H_3C-OH \; \rightleftharpoons \; H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3 \qquad (1)$$
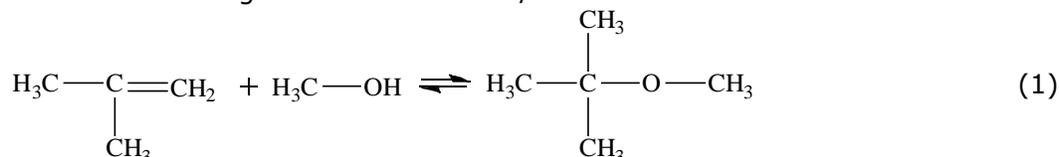
Kinetic parameters of the reaction (1) have been considered in the article [12], according to which reaction rate of MTBE forming can be express as:

$$r = k_f \cdot \left(\frac{\alpha_{IB}}{\alpha_{MeOH}} - \frac{\alpha_{MTBE}}{K_{eq}\alpha_{MeOH}^2} \right) \qquad (2)$$

where $k_f = 3.67 \cdot 10^{12} \cdot e^{\frac{-11110}{T}}$ - forward reaction constant [12]; $K_{eq} = e^{(-16.3 + \frac{6820}{T})}$ - chemical equilibrium constant [12]; $\alpha_{IB}, \alpha_{MeOH}, \alpha_{MTBE}$ – activity coefficients of isobutylene, methanol and MTBE respectively.

The main reaction (1) is frequently followed by side reactions:
Dimerization of isobutylene:

$$H_3C-\underset{\underset{CH_3}{|}}{C}=CH_2 \; + \; H_3C-\underset{\underset{CH_3}{|}}{C}=CH_2 \; = \; H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=\overset{\overset{CH_3}{|}}{C}-CH_3 \qquad (3)$$

Hydration of isobutylene:

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}=CH_2 \;+\; H_2O \;=\; H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \qquad (4)$$
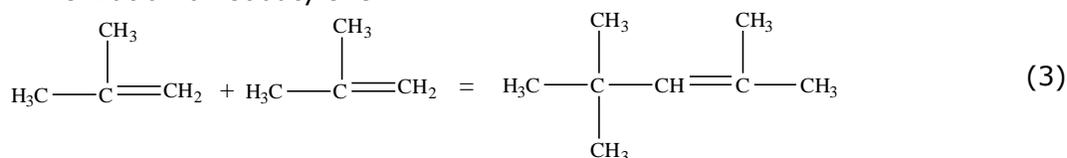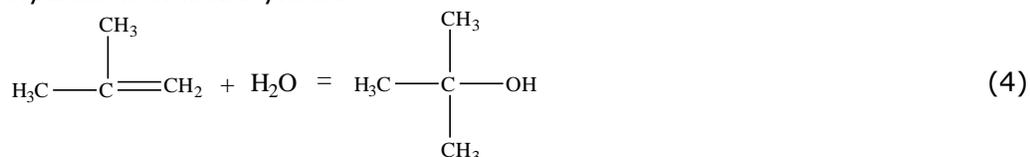
Intermolecular dehydration of methanol with formation of dimethyl ether and water:

$$2\; H_3C-OH \;\rightleftharpoons\; H_3C-O-CH_3 \qquad (5)$$

The main feature of the process is usage of hydrocarbon feedstock of various composition – IIF (isobutene-isobutylene fraction) and BIF (butylene-isobutylene fraction). Thus, side products form due to reaction between hydrocarbons $C_4 - C_5$ from initial fraction and methanol:

$$H_3C-\underset{H}{\overset{}{C}}=\underset{H}{\overset{}{C}}-CH_2 + H_3C-OH \rightleftharpoons H_3C-\overset{H_2}{C}-\underset{\underset{CH_3}{|}}{\overset{H}{C}}-O-CH_3 \qquad (6)$$

$$H_2C=\underset{H}{\overset{}{C}}-\underset{H}{\overset{}{C}}=CH_2 + H_3C-OH \rightleftharpoons H_3C-\underset{H}{\overset{}{C}}=\underset{H}{\overset{}{C}}-\overset{H_2}{C}-O-CH_3 \qquad (7)$$
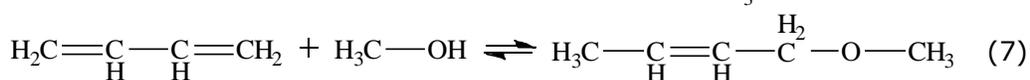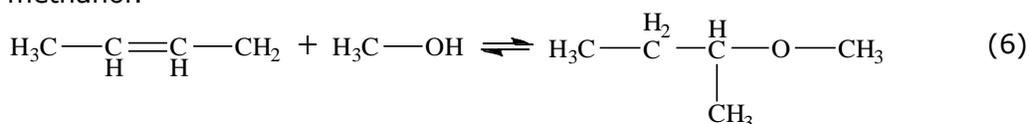
In order to reduce side ethers yield, diolefins concentration in the feedstock is limited by special requirements [24].

The flowsheet of one production line of MTBE synthesis is presented in Figure 1 [24].
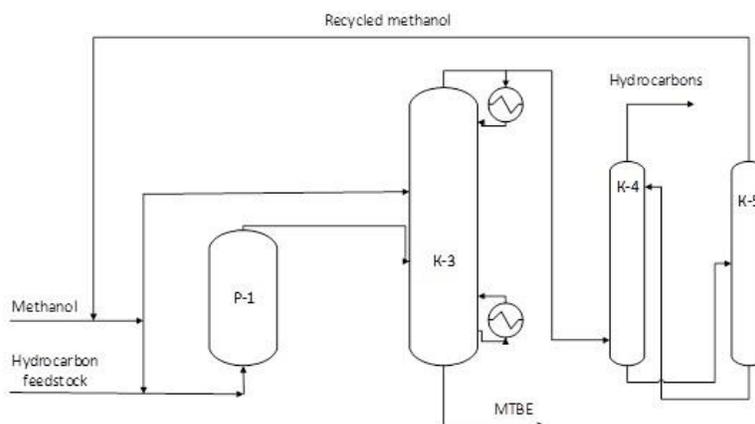

Figure 1. MTBE production flowsheet proposed by Research Institute "Yarsintez"
P-1 – reactor of evaporative-adiabatic type; K-3 – reactive distillation column; K4 – water washing column; K-5 – column of methanol recovery.

The feedstock streams are: IIF (composition is given in Table 1); BIF (composition is given in Table 1); methanol [25]. High product yield is provided by catalysts KU-2FPP or KIF-T.

KU-2FPP is combustible solid, chemical composition of which involves polypro-pylene and sulfonated styrene copolymer with divinylbenzene. KIF-T is also combustible solid and it consists of a composition of polypropylene and sulfonated styrene copolymer with divinyl-benzene, acrylonitrile and sulfonated polyethylene.

Table 1. Feedstock composition

	IIF, %mass	BIF, % mass		IIF, %mass	BIF, % mass
Propane	0.18	0.10	Isobutylene	41.48	35.73
Isobutane	57.21	8.64	Butadiene	0.04	0.28
N-butane	0.63	19.55	Σ of butylenes	0.46	35.69

The operating parameters of the feedstock are shown in Table 2.

Table 2. Feedstock operating conditions

	Hydrocarbon feedstock	Methanol
Flow-rate, ton/h	0.027	0.006
Temperature, °C	79.5	33
Pressure, kPa	759.938	911.925

Material balance for MTBE production is made for 239,636 tones output per 2016 year and given in Table 3. The Table 3 shows that productive capacity of the unit is 28.29 tones per hour with conversion of isobutylene 98%.

Table 3. Material balance

Input				Output			
	Components	% mass	tones per hour		Components	% mass	tones per hour
	Isobutene-isobutylene fraction				1.MTBE	100.00	28.29
1	Propane, propylene	0.20	0.08		2.Wasted hydrocarbon fraction		
2	Iso-butane	56.10	21.46	1	Propane, propylene	0.33	0.09
3	Isobutylene	41.20	15.76	2	Iso-butane	79.78	22.07
4	N-butane	1.40	0.54	3	Isobutylene	6.50	1.84
5	N-butylenes	1.10	0.42	4	N-butane	11.88	3.36
	Total	100.00	38.25	5	N-butylenes	1.51	0.43
	Butylene-isobutylene fraction				Total	100.00	28.26
1	Propane, propylene	0.21	0.02		3.Losses	100.00	0.05
2	Iso-butane	7.61	0.61				56.60
3	Isobutylene	39.20	3.14		Total	100.00	8.00
4	N-butane	16.28	1.30		Methanol	100.00	10.35
5	N-butylenes	36.70	2.94		Total feedstock		56.60

According to the scheme in the Figure 1, the main units for the synthesis are the reactor P-1 and the RD column K-3. Therefore, proper simulation of kinetic, mass transfer, hydrodynamic features of these units, which are to be specified as nearly as possible to industrial conditions, provides successful modeling on the whole.

2.2 Selecting fluid package and modeling of kinetics

The first important step is chemical reaction modeling. After defining all the substances involved in the main and side chemical reactions, we need to choose the most suitable fluid package. The researchers of Tomsk polytechnic university have studied vapor-liquid equilibrium in the system "isobutylene – n-butene – MTBE – methanol" and arrived at the conclusion that the most appropriate fluid package for thermodynamic calculations of simple ethers is package *Wilson* [26].

Kinetic simulation of MTBE synthesis in Aspen HYSYS® requires selecting type of chemical reaction. The main reaction described by kinetic equation (2) can be defined in HYSYS® in a suitable manner using type *kinetic*. Kinetic type allows specifying forward and backward reaction rates and does not enable to describe catalyst parameters, which is obvious disadvantage for a heterogenic process simulation.

The forward and backward reaction rate constants are represented as temperature functions, generally expressed as:

$$k = A \cdot e^{\frac{-E}{RT}} \cdot T^{\beta},$$

(8)

where A – pre-exponential factor; k – reaction rate constant; E – activation energy, J/mole; $β$ – constant of the extended Arrhenius equation; R – universal gas constant, J/(mole·K); T – absolute temperature, K.

For the forward and backward reactions $β$ is assumed to be 0. To bring the kinetic equation nearer to heterogenic process, we expressed the pre-exponential factors for forward and backward reactions with regard to catalyst mass parameter M_c [12]:

$$A^* = AM_c, \tag{9}$$

where A^* – pre-exponential factor in HYSYS®.

The Table 4 shows kinetic parameters of the main MTBE synthesis reaction specified in HYSYS®.

Table 4. Kinetic parameters of the reaction (1)

Parameter	Value	Parameter	Value
Type	kinetic	Phase of reaction	Liquid
Base component	Isobutylene		
Forward reaction		Backward reaction	
A	$7.34 \cdot 10^{20}$	A`	$7.88 \cdot 10^{15}$
E, J/mole	92324	E`, J/mole	149000

As the product yield is sufficiently high, side reactions (3) – (7) do not influence on the process significantly. At the same time, without necessary kinetic data of reaction behavior on the catalyst, it is appropriate to use equilibrium type for side reaction simulation.

2.3. Simulation of the main units

The main units for the MTBE synthesis are the reactor and the RD column. The reactor is a hollow cylindrical vessel with fixed-bed catalyst (P-1 in Figure 1). The screenshot of the reactor modeling is given in Figure 2.
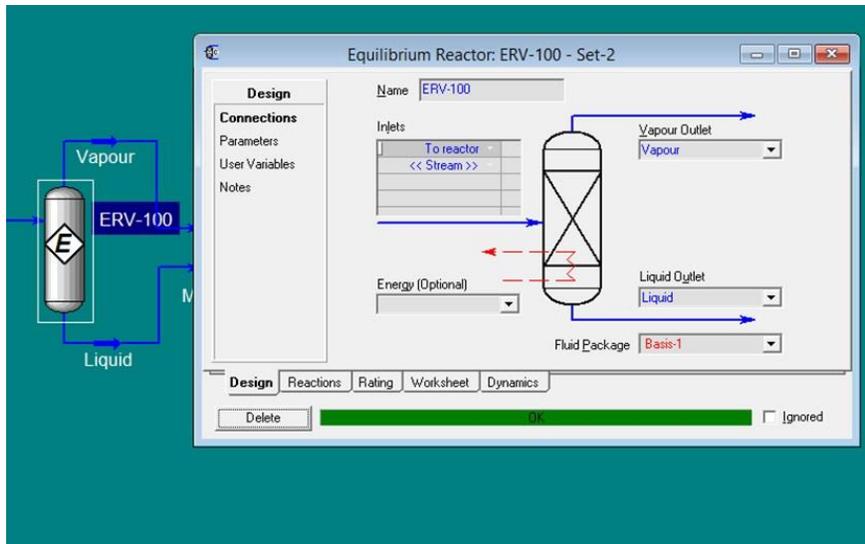
Figure 2. The MTBE synthesis reactor modeling in Aspen HYSYS®

Specifications of the reactor according to production documents are given in Table 5.

Table 5. Specifications of the MTBE synthesis reactor

Parameter	Value	Parameter	Value
Volume	75.6 m³	Pressure	1300 kPa
Diameter	3000 mm	Temperature	100°C
Length	16680 mm		

The reactive distillation column includes three sections (see Figure 3): rectifying section, reactive section and stripping section.
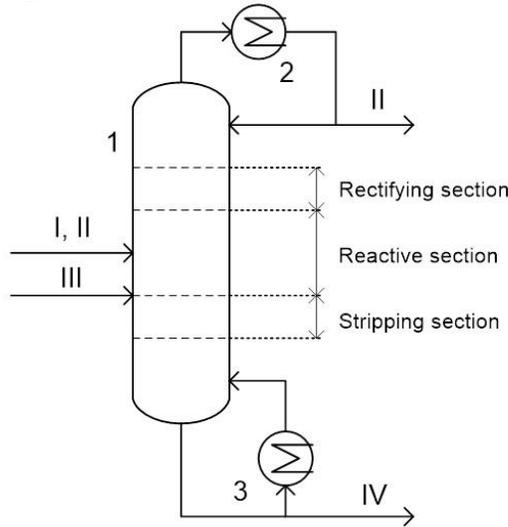

Figure 3. The reactive distillation column (I – isobutylene; II – n-butylenes; III – methanol; IV – MTBE; 1 - reactive distillation column; 2 - total condenser; 3 – reboiler)

Specifications of the reactive distillation column are given in Table 7.

Table 7. Specifications of the reactive distillation column

Parameter	Value	Parameter	Value
Pressure	1000 kPa	Overhead temperature	42 °C
Diameter	2200 mm	Number of trays	80
Height	58650 mm	Feed tray	29
Bottom temperature	135 °C		

The reactive distillation column was simulated in Aspen HYSYS® (see Figure 4).
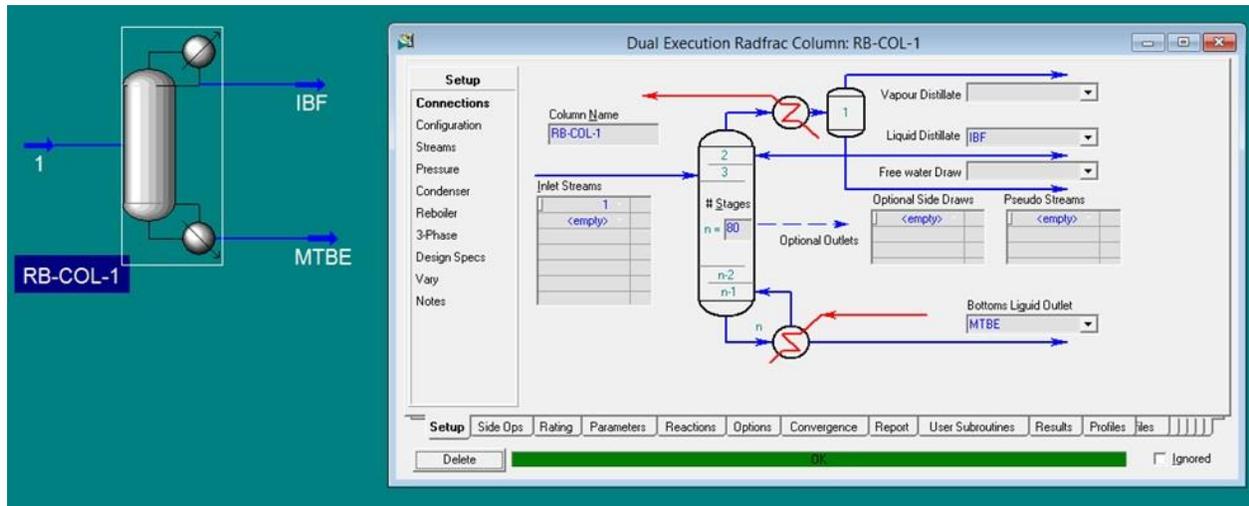
Figure 4. The reactive distillation column in Aspen HYSYS®

The last versions of Aspen HYSYS® make possible to use equilibrium models as well as non-equilibrium models for simulation of the reactive distillation columns. The main assumption of the equilibrium models is phase equilibrium, in this case calculation of the heat- and mass-transfer coefficients is not required. Due to its clearness equilibrium models are successfully

used in designing, research and control of the reactive distillation columns. It is believed that this type of models is suitable for description of the azeotropic polystable systems in reactive distillation columns, but according to some research papers [27] careful calculations of the heat- and mass-transfer could be very important for this kind of simulation.

Non-equilibrium (Rate-based) model was used for the reactive distillation column modeling because it allows taking into account kinetic parameters (Table 4).

The aggregate scheme of MTBE synthesis is presented in Figure 5. The developed model was verified, and then we made some prediction and optimization calculations.
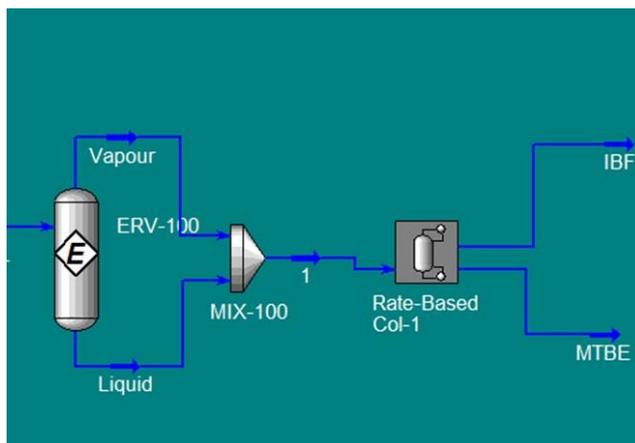

Figure 5. HYSYS® scheme of the MTBE production unit

2.4. Model verification

The model was verified by comparing the calculation results with the data of industrial facility of MTBE synthesis provided for January 2016. For that period of time hydrocarbon feedstock included IIF (isobutene-isobutylene fraction, composition is given in Table 1) and methanol.

The composition of the MTBE flow from the RD column bottom is given in Table 8. The composition of the wasted hydrocarbon fraction is presented in Table 9. Calculated values are shown in comparison with the same real values.

Table 8. Composition of the MTBE flow from the RD column bottom

	MTBE	Methanol	Isobutylene	MsBE	Water	Butylenes	Isobutane
Plant data, % mass	98.70	0.06	0.37	0.01	0.00	0.76	0.10
Calculation result, % mass	94.51	0.11	0.58	0.00	0.00	0.57	4.23

MsBE-methyl-*sec*-buthyl ether

As shown in Table 8, the error of MTBE content calculation is 4.2 %. Total calculated content of the by-products does not exceed 1 %, excepting isobutane. Considerable error of the isobutane content estimation is connected with imperfect calculation of the distillation process.

Table 9. Composition of the wasted hydrocarbon fraction

|	Isobutane	N-butane	Isobutylene	Butadiene	Methanol	Butylenes	Propane
Plant data, % mass	96.85	1.12	0.76	0.07	0.00	0.88	0.32
Calculation result, % mass	94.45	0.78	3.91	0.05	0.00	0.50	0.31

According to Table 9, the error of isobutane content calculation is 2.5 %. Therefore, the developed model provides good accuracy of calculation and could be used for the MTBE synthesis process optimization.

2.5. Optimization of the MTBE synthesis process

The hydrocarbon feedstock of the MTBE synthesis process can be changed from IIF to BIF and back, so the influence of feedstock composition is significant for the process efficiency. For that reason optimization calculations should take into account both types of hydrocarbon feedstock, IIF and BIF (see Table 1).

We investigated how reflux ratio (R) and methanol flowrate influence MTBE concentration in the main product flow. Reflux ratio was varied from 0.6 to 1.0 and methanol flowrate – from 5.000 ton/h to 6.800 ton/h.

The MTBE content as a function of reflux ratio is presented in Figure 6. According to Figure 6, the MTBE content increases with reflux ratio growth, optimal R is 0.75 for IIF hydrocarbon feedstock and 0.8 for BIF hydrocarbon feedstock. The MTBE content as a function of methanol flowrate is presented in Figure 7.
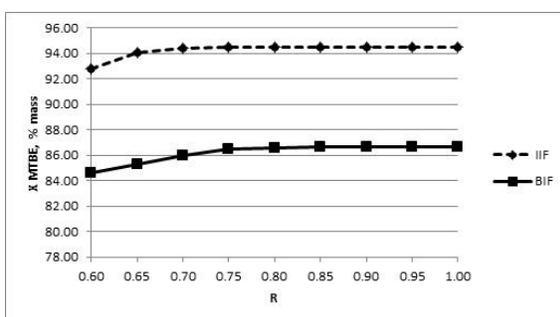

Figure 6. MTBE content as a function of reflux ratio
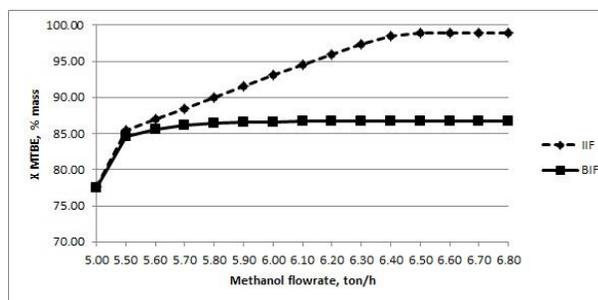
Figure 7. MTBE content as a function of methanol flowrate

As represented in Figure 7, the MTBE content increases with methanol flowrate growth, optimal flowrate is 6.500 ton/h for IIF hydrocarbon feedstock and 6.000 ton/h for BIF hydrocarbon feedstock. The optimal values of reflux ratio and methanol flowrate for the different types of hydrocarbon feedstock are given in Table 10. The calculated optimal values are shown in comparison with the same real values.

Table 10. The optimal values of reflux and methanol flowrate

Hydrocarbon feedstock type		Reflux ratio	Methanol flowrate, ton/h	MTBE content, % mass
IIF	Plant data	0.90	6.100	94.51
	Optimal value	0.75	6.500	98.86
BIF	Plant data	0.90	6.100	86.66
	Optimal value	0.80	6.000	86.61

As shown in Table 10, the MTBE content is greater in case of IIF usage because content of isobutylene is 5 % higher in IIF then in BIF. In this respect, operating parameters for BIF as hydrocarbon feedstock should be corrected in order to provide decrease of thermal charge and feedstock flowrate.

Summary

1. Modern approaches to reactive distillation modeling are based on complicated mathematical models and require special software. Aspen HYSYS® enables to create stable and dynamic models of equilibrium and rate-based processes. At the same time, there are some limitations in specification of a catalyst of heterogeneous reaction.

2. The product line of MTBE synthesis within the industrial plant was simulated in Aspen HYSYS®. Calculation error does not exceed 5 % for the main product concentration, thus we considered the model as adequate and used it for further studies.
3. The main feature of industry-scale MTBE production is changes in hydrocarbon feedstock composition. The feedstock composition study showed that usage of IIF is more preferable than BIF as MTBE content in the main product stream is 12 % higher for IIF in comparison to BIF. Optimization calculations of the reflux ratio and the methanol flowrate lead us to the conclusion that: for IIF feedstock – optimal reflux ratio is 0.75, methanol flowrate – 6.500 ton/h; for BIF feedstock – optimal reflux ratio is 0.80, methanol flowrate – 6.000 ton/h.

Acknowledgements

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