

# Parametric Optimization of a Reactive Distillation Column for the Ethyl *Tert*-Butyl Ether Production

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Received: 02 March 2023, Accepted: 11 September 2023, Published online: 08 March 2024

## Abstract

Combined processes in chemical industry are of current increasing interest, since they present a feasible solution for capital and operating expenses optimization. Multiplicities, which are specific to combined processes, cause certain control and design difficulties, thus, parametric sensitivity analysis and defining the range of existing multiplicities are the necessary part of the sustainable design and development of the combined process. Parametric and design optimization is the way of decreasing capital and operational costs. The paper discusses optimization of the design and operating parameters of an ethyl-*tert*-butyl ether synthesis reactive distillation column. The research aims to perform a parametric sensitivity analysis and explore existent multiple steady states of the process. The areas of multiple steady states are established, the optimal column design is developed, the optimal operation modes are determined. The procedure suggested in the study is universally applicable for design and optimization of other reactive distillation processes.

## Keywords

mathematical model, optimization function, parametric sensitivity, reactive distillation synthesis, ethyl-*tert*-butyl ether

## 1 Introduction

Traditionally, a chemical technology process involves chemical reaction and distillation of end products arranged sequentially in separate units. Reactive distillation (RD) represents a way to intensify the synthesis process by carrying out both chemical reaction and distillation in the same column [1]. Fig. 1 shows the path flow diagrams of both traditional and reactive distillation processes.

Reactive distillations can be applied to systems with the following conditions:

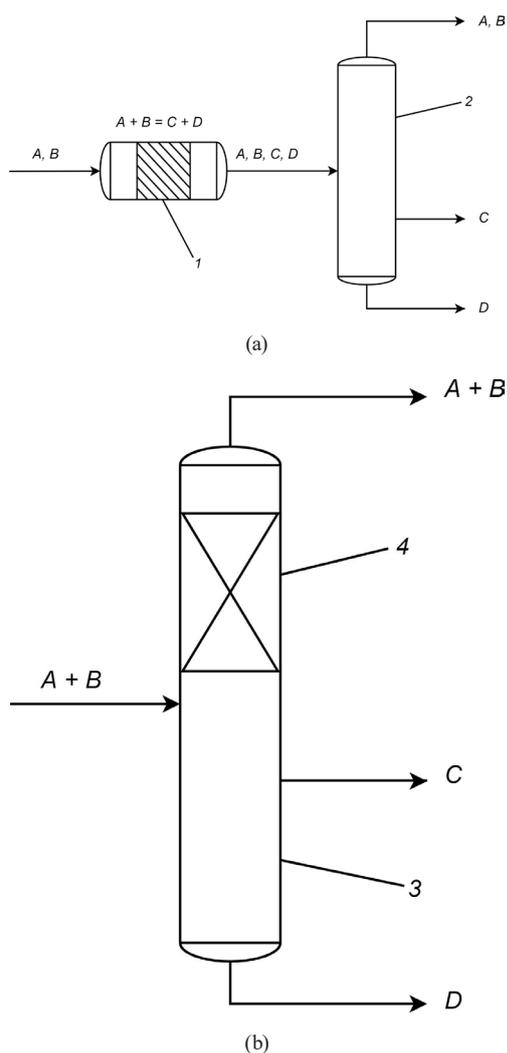
1. chemical reaction and separation of products occur in the same range of temperatures and pressures,
2. reactants and products have sufficiently large difference in relative volatilities [1].

The functional integration of reaction and separation offers significant advantages:

1. capital and operating costs are reduced by 15 to 80% due to reduction of the number of individual units used and, additionally, the reliability of the arrangement is increased due to using less equipment [2];

2. heat emitted in exothermic reactions decreases the amount of energy consumed in evaporation;
3. constant product removal and recycle of reactants make it possible to overcome thermodynamic equilibrium limits and achieve close to complete reagent conversion [3–4].

Reactive distillation has been used successfully in the esterification processes. A classic example of reactive distillation is Eastman Chemical's production process of 1980, in which the traditional reactor and nine columns were replaced by a single reactive distillation column, thus reducing capital and operating costs by 5 times [2]. RD is widely implemented in the syntheses of ethers, such as methyl-*tert*-butyl (MTBE), methyl-*tert*-amyl (TAME) and ethyl-*tert*-butyl (ETBE) ethers, which are used as high-octane components of motor gasoline [5]. CDTECH holds licenses for RD production processes of these ethers (CDMtbe®, CDTame® and CDEtbe® respectively) as well as other processes including hydrogenation, desulfurization, isomerization and alkylation of oil fractions [2, 6–7].



**Fig. 1** Schemes of reaction and distillation; (a): sequential; (b): combined; A, B: input components; C, D: products of the reaction; 1: reactor; 2: distillation column; 3: reactive distillation column; 4: reactive section

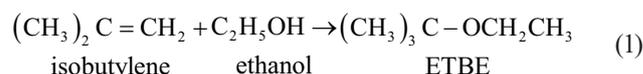
By 2022, the number of reactive distillation applications exceeded 200 industrial facilities [2]. For example, reactive distillation unit is considered as offering lower energy consumption in comparison with conventional distillation, and economically sound for biodiesel production from palm fatty acid distillate [8]. Another work [9] provides a comparison between a conventional and a reactive distillation technology of biodiesel production from technical and environmental standpoints. For some feedstocks, the innovative combined unit outperforms the classic approach in six out of nine environmental impact categories. Reactive distillation syntheses are actively studied not only experimentally, but also by means of validated simulations based on kinetic and thermodynamics models developed for various processes [10]. A detailed review of more than

100 industrially important processes with RD is presented in [5]. Compared to other homologues, ethyl-*tert*-butyl ether (ETBE) is of particular interest as it is produced from ethanol, which, in contrast to methanol synthesized from natural gas, can be obtained from renewable sources, such as biomass, molasses and agricultural feedstocks. In Hungary ETBE production from bioethanol began during the second half of 2005 by the Hungarian oil company MOL [11]. Nippon Oil Corp. began producing ETBE from bioethanol in 2009 [12]. Being in demand in industry, the integration of chemical transformation and reaction mixture separation leads to the use of special methods for design and development of optimal process configuration. Review of the methods is presented in [13]. Design methods are classified into three groups: graphical [14–16], heuristic [17–18], and optimization [19–20]. The static analysis by graphical methods determines the feasibility of RD process, limiting steady states that provide the maximum yield of the end-product over the entire range of feed compositions; separation direction (direct or reverse); localization and number of feed inputs, localization of the reactive section. Optimization methods combine mathematical modeling of processes with numerical optimization algorithms and, as the result, offer a deterministic and systematic decision-making tool. The object of optimization is the principal model of the equipment or the flow diagram as a whole. In the present study we propose a new indicator in a form of target function. The developed target function enables to achieve maximal product purity and conversion simultaneously. The main feature of the new indicator is its versatility, thus, it is possible to use it for various mass transfer and combined processes. The approach provides an integration of process simulation environment with parametric optimization, which is not limited to a target function gradient and enables to take into account integer variables, such as number of trays, locations of feed or recycles, etc. The aim of this research is to develop a model of ethyl-*tert*-butyl ether reactive distillation synthesis process, to analyze process and design parametric sensitivity, study of multiple steady states and design parameters optimization.

## 2 Theoretical analysis

### 2.1 Underlying chemistry

The main ETBE synthesis route is the reaction between isobutylene and ethanol. The reaction proceeds in the liquid phase with an acid catalyst [21].



Equation (1) is exothermic  $\Delta H^\circ = -61,83$  kJ/mol [22]) and limited by thermodynamic equilibrium; conversion of the equimolar "ethanol: isobutylene" mixture is 84.7 mol % at 70° C [21].

In industry, isobutylene is available as a component of butene mixture (C4 fraction), the sources of which can be units of fluidized catalytic cracking, pyrolysis or isobutane dehydrogenation [21]. Ethanol is used as a one-component stream.

The catalyst is an ion-exchange acid resin of a macro-crosslinked, sulfonic type (a copolymer of polystyrene and divinylbenzene). The Amberlyst–15 is used most widely; the performance of the catalyst is given in [23].

## 2.2 VLE conditions and methods

Physical properties of the substances in C4/ETBE/ethanol systems differ significantly. Therefore, the reactive mixture of the process has a highly non-ideal behavior and can form azeotropic mixtures. So, a careful selection of an appropriate thermodynamic method is an important step in this study.

The UNIFAC model was used for the simulation of the liquid phase because it predicts the non-ideal behavior of C4/ETBE/ethanol mixtures and allows to avoid regression analysis in order to obtain binary interaction coefficients.

The azeotropic mixtures in C4/ETBE/ethanol system at different pressures are described in Table 1.

According to Table 1, there is one "ethanol – ETBE" azeotrope predicted under the conditions 950 kPa, 66.6 °C with a 59 : 41 "ethanol : ETBE" mass ratio [25]. The "ethanol: ETBE" ratio in the column feed is much lower – 6.1 : 43.3 (Table 2), which prevents the azeotrope to form under simulation conditions. The simulation of the vapor phase is

**Table 1** Azeotropic data in C4/ETBE/ethanol system

Boiling points of the pure components at 101 kPa (°C)			
ETBE	Ethanol	Isobutylene	1-butene
72.8	78.4	6.9	6.6
Azeotropic mixtures			
Experimentally observed			
Mixture	$x_{ethanol}$ at 101 kPa (mass %) [24]	$x_{ethanol}$ at 950 kPa (mass %) [21]	$x_{ethanol}$ at 1400 kPa (mass %) [21]
Ethanol – isobutylene	No data	No data	0.94
Ethanol – 1-butene	No data	No data	No data
Ethanol – ETBE	21	No data	No data
Predicted by UNIFAC [21]			
Ethanol – isobutylene	No azeotrope	No azeotrope	1.25
Ethanol – 1-butene	No azeotrope	No azeotrope	1.45
Ethanol – ETBE	38	59	66

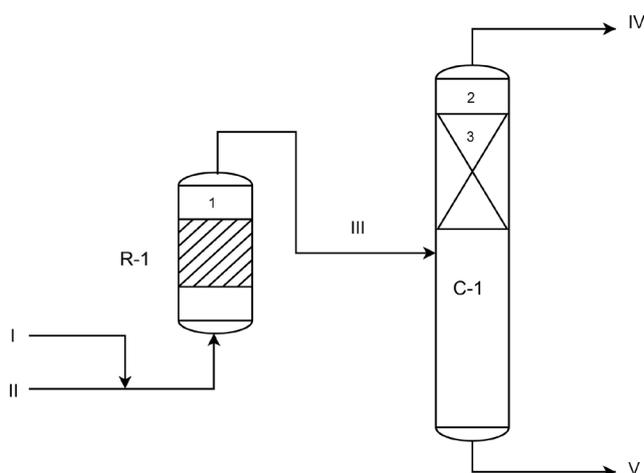
presented by Soave–Redlich–Kwong equation (SRK), which can properly model the behavior of both long-chain molecules, as well as more polar molecules.

## 2.3 Process flow diagram

Fig. 2 shows a basic flow diagram of the ETBE synthesis by reactive distillation. The purified C4 fraction I is mixed with pure ethanol II and fed to the reactor R–1, where ETBE is formed with isobutylene conversion of 85 mol %. The shell-and-tube reactor is operated under isothermal conditions. The reaction mixture passes through the tube space. Reaction heat is removed by circulating water passing through the shell side. The products from the reactor R–1 enter the reactive distillation column C–1. The column

**Table 2** Modeling parameters

Feed stock	
Composition (mass %)	ETBE (43.3); ethanol (6.1); isobutylene (6.0) n-butylenes (44.6 as 1-butene)
Temperature	303.15 K
Pressure (absolute)	950 kPa
Flow rate	0.76 L/s $\equiv$ 29.8 kg/h
Assumptions	
Model type	Phase equilibrium
Liquid phase description	Strict non-ideal
Thermophysical phase models	Liquid – UNIFAC Vapor – SRK
Reactions (mode)	Kinetic
Reaction mixture (reacting phase)	Liquid
RD column design	
Feed composition	Reaction mixture from the outlet of the first isothermic reactor
Inlet points	Single
Side takeoffs	None
Theoretical trays in total	10
Condenser	Tray 1
Reboiler	Tray 10
Condenser	Full
Reboiler	Partial
Reactive section	Trays 3–5
Catalyst load	6 kg per tray
Feed tray	Tray 6 (feed above tray)
Reflux	Single, on tray 2
Top pressure	950 kPa (abs.), pressure loss 0 kPa
Reflux ratio	Varies
Reboiler heat load	Varies



**Fig. 2** ETBE reactive distillation synthesis flow diagram; I: fraction C4; II: ethanol; III: products from the reactor; IV: mixture of inert hydrocarbons C4 with isobutylene and ethanol; V: ETBE; 1: reactor; 2: reactive distillation column; 3: reactive section

is equipped with trays, some of which are loaded with catalyst. In the column isobutylene conversion and ETBE recovery occur simultaneously, with ETBE in the form of the bottom product of more than 95 mass % purity (V); some of the unreacted ethanol also occurs in this stream. Distillate IV is a mixture of inert hydrocarbons of feed fraction C4 with isobutylene and ethanol.

## 2.4 Reaction mechanism and kinetics

The reaction mechanism in the isobutylene-ethanol system involves the adsorption of ethanol on two catalyst sites and of isobutylene adsorption on an adjacent one. The process is limited by the reaction between the adsorbed substances; the final stage is the product desorption. The reaction rate equation is based on the Langmuir-Hinshelwood-Hougen-Watson model. The kinetic model resulting from studies on the Amberlyst 15 catalyst is represented by the following Eq. (2)–(5) [21, 26]:

- Reaction rate:

$$r_{\text{ETBE}} = m_{\text{cat}} \times k_{r,\text{ETBE}} \frac{a_{\text{ethanol}}^2 \times \left( a_{\text{isobut}} - \frac{a_{\text{ETBE}}}{K_{\text{ETBE}} \times a_{\text{ethanol}}} \right)}{\left( 1 + K_{A,\text{ethanol}} \times a_{\text{ethanol}} \right)^3}; \quad (2)$$

- Reaction-rate constant:

$$k_{r,\text{ETBE}} = 2.0606 \times 10^{12} \exp\left(-\frac{60.4 \times 10^3}{RT}\right); \quad (3)$$

- Adsorption constant:

$$\ln K_{A,\text{ethanol}} = -1.0707 + \frac{1323.1}{T}; \quad (4)$$

- Chemical equilibrium constant:

$$\ln K_{\text{ETBE}} = 10.387 + \frac{4060.59}{T} - 2.89055 \ln T - 0.0191544T + 5.28586 \times 10^{-5} T^2 - 5.32977 \times 10^{-8} T^3. \quad (5)$$

It is assumed in the reaction rate expression for ETBE (Eq. (2)) that ethanol occupies most of the catalyst surface [21], so dimerization and hydration of isobutylene are practically excluded.

## 3 Calculation part

### 3.1 Mathematical modeling of the reactive distillation process

Simulation is a powerful tool for a process flow diagram (PFD) analysis and optimization which allows to compare energy consumption, investments and operation cost for various alternatives along with production data such as recovery or/and product quality. For example, in [27] the authors utilized energy and cost effectiveness, acid concentration in vapor and outlet temperature for the process of spend sulfuric acid recovery by simulation in Aspen Plus v. 9.1. [28]

Another way is a conceptual design based on fundamental conservation and thermodynamic principles [29].

To perform parametric optimization, we have modified a RD column taking as reference the column described in the work by Sneesby et al. [21], changing some characteristics in order to achieve the required product purity with a high isobutene conversion.

A model of an RD column has been developed in Aspen Plus 10.1 [30]. The output from the isothermic reactor at 80% isobutylene conversion was taken as the feed stream. The initial data and modeling assumptions are presented in Table 2.

### 3.2 Development of the target function

Operating costs are determined mainly by the heat supply for evaporation and the costs of cooling and pumping the reflux flow, therefore, their impact on the performance of the column was analyzed.

The heat supply is expressed through the heat load of the reboiler ( $QN$ ).

The costs of cooling and pumping the reflux flow are expressed in terms of the reflux ratio ( $RR$ ).

Equation (6), which takes into account the degree of conversion for isobutylene ( $\varepsilon_{isobut}$ ) and the purity of the resulting ETBE ( $x_{ETBE}$ ) simultaneously, shows column performance and is taken as a target function:

$$\Psi = (1 - x_{ETBE})^2 + (1 - \varepsilon_{isobut})^2 = f(QN, RR). \quad (6)$$

The conversion is defined as:

$$\varepsilon_{isobut} = \frac{n_{inlet} - n_{outlet}}{n_{inlet}}. \quad (7)$$

where  $n_{inlet}$  and  $n_{outlet}$  are the molar flowrates of isobutylene at the inlet and outlet of the reactive distillation column, respectively.

### 3.3 Parametric optimization algorithm

Parametric optimization is carried out in two consecutive stages. At the stage of the operational parameter study, an analysis of  $x_{ETBE}$  and  $\varepsilon_{isobut}$  parametric sensitivity to reboiler heat load and reflux ratio is performed. At the same time, this analysis reveals possible multiple steady states. The functional relationship between the parameters,  $QN$  and  $RR$  vary in the significant range for industrial application:

$$QN = 7.3 - 9 \text{ kW}, \quad RR = 4.5 - 5.25.$$

At the stage of the design parameter study, we perform a sensitivity analysis of the target function  $\Psi$  to three aspects: reboiler heat load, reflux ratio and column topology. This analysis reveals the target function minimum, as well as the corresponding minimum energy requirements for optimal operation columns.

To find the global minimum, the range of  $QN$  and  $RR$  values is expanded as follows:

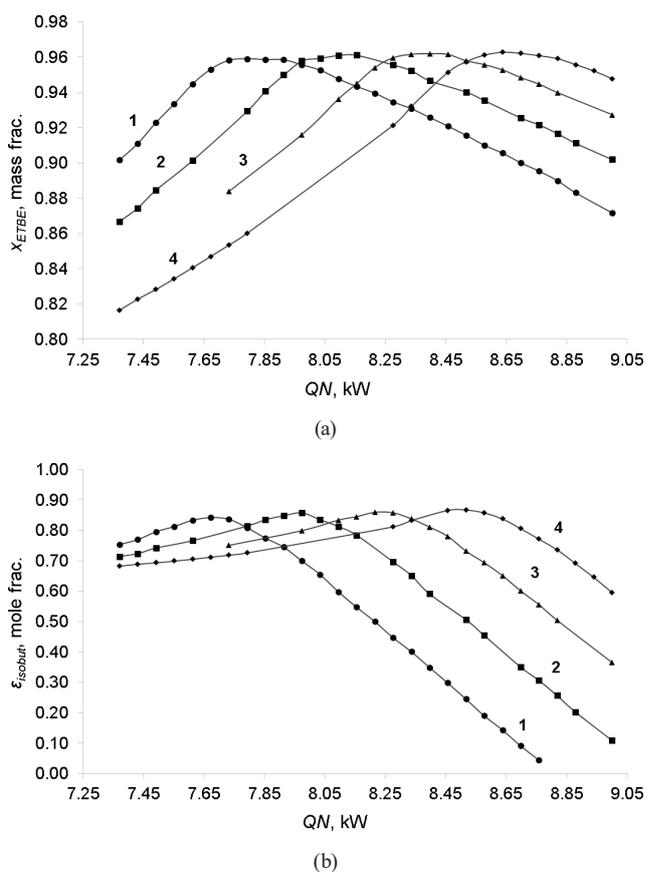
$$QN = 8 - 17 \text{ kW}, \quad RR = 5 - 12.$$

## 4 Results and discussion

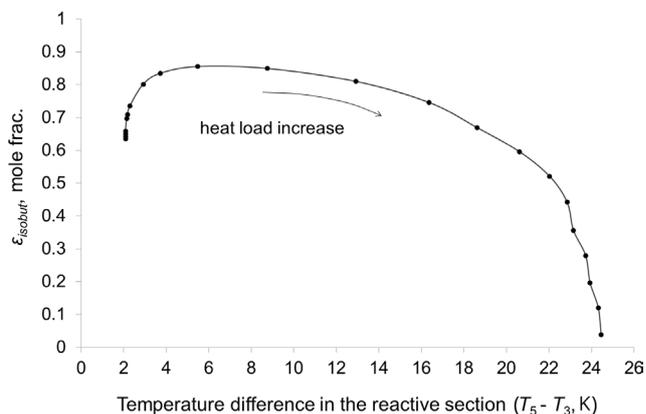
### 4.1 Operational parameter study

The results of target function study as functions of the operational parameters are given in Figs. 3 and 4.

As shown in Fig. 3, it is possible to increase  $x_{ETBE}$  and  $\varepsilon_{isobut}$  simultaneously. This point corresponds to a specific combination of heat load and reflux ratio, where the target Eq. (6) reaches its minimal value. Fig. 4 represents an increase in the isobutylene conversion with reducing in the temperature difference on the trays of the reactive section of the column with the maximum near  $T_5 - T_3 = 5 - 6$  K. Consequently, the increase of reflux on these trays or the supply of reactive zone with cold



**Fig. 3** The dependence of the target function parameters on the reflux ratio and the reboiler heat load; (a): ETBE purity; (b): isobutylene conversion; 1:  $RR = 4.5$ ; 2:  $RR = 4.75$ ; 3:  $RR = 5$ ; 4:  $RR = 5.25$



**Fig. 4** Isobutylene conversion versus the temperature difference on the 3<sup>rd</sup> and 5<sup>th</sup> trays of the reactive section.  $RR = 5$ , the arrow indicates the direction of  $QN$  increase

ethanol is a way to increase the conversion of isobutylene by temperature control. Figs. 3 and 4 also show the nonlinear nature of reactive distillation, in which multiple heat loads are possible at a constant degree of conversion and purity of ETBE. The results are presented in Tables 3 and 4. The multiplicity of heat loads directly affects the economic efficiency of the process, since

the same performance can be achieved with less heat consumption. Energy savings reach 16% with a purity of ETBE 0.9, and 10.4% with the isobutylene conversion degree of 0.7. The reflux ratio is 4.75 (Tables 3 and 4).

### 4.2 Design parameter study

To determine the influence of the design parameters, we studied the dependence of the target function  $\Psi$  on the heat load and the reflux ratio with an increased size of the reactive section and the reflux recycle to the reactive section. The considered structures are shown in Fig. 5. Fig. 6

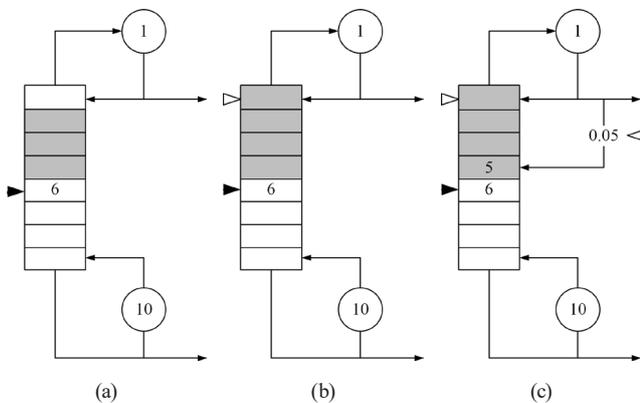
**Table 3** Heat load multiplicity for constant ETBE purity

ETBE purity	Maximum $QN$ (kW)	Minimum $QN$ (kW)	Difference (%)
<i>RR = 4.5</i>			
0.90	8.70	7.37	15.26
0.92	8.46	7.49	11.10
0.94	8.16	7.61	6.24
<i>RR = 4.75</i>			
0.90	9.00	7.61	15.95
0.92	8.70	7.79	10.40
0.94	8.52	7.85	7.63

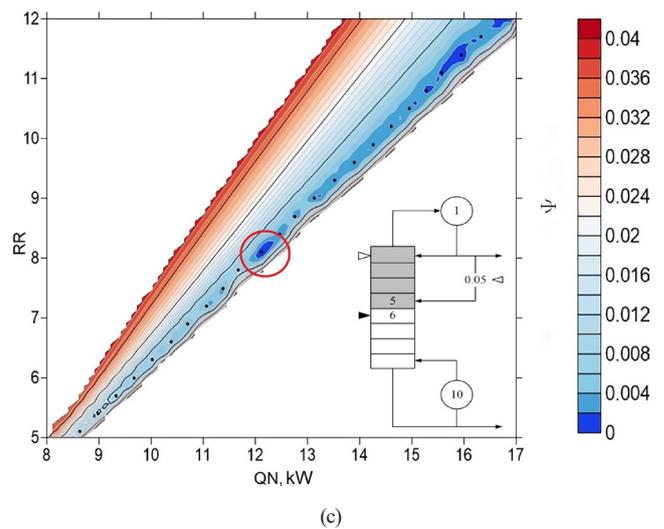
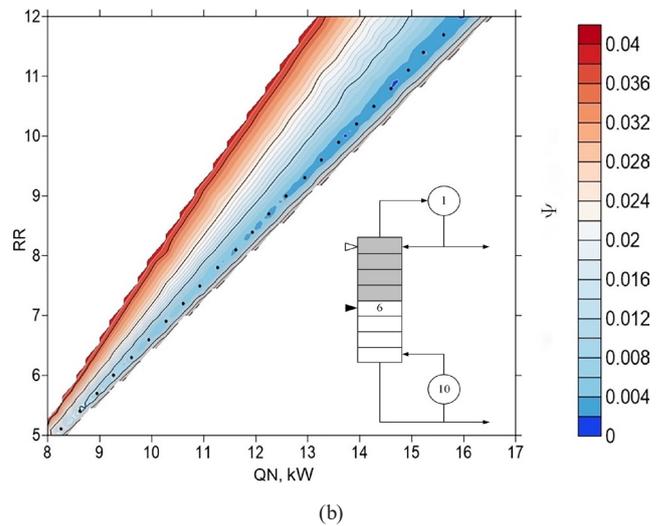
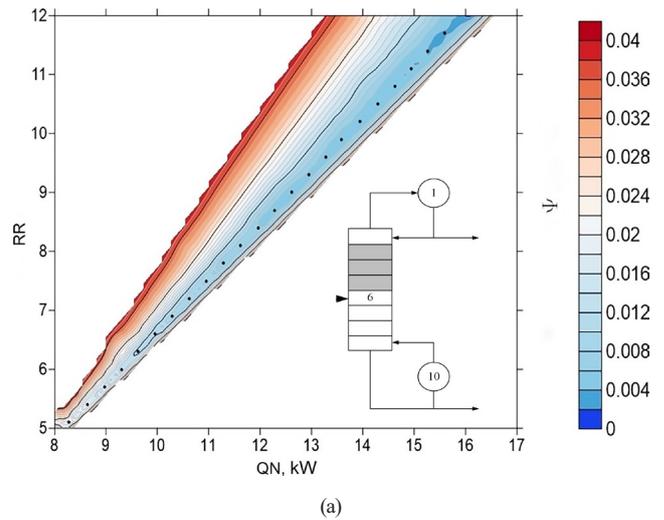
**Table 4** Heat load multiplicity for constant isobutylene conversion

Isobutylene conversion, mole frac.	Maximum $QN$ (kW)	Minimum $QN$ (kW)	Difference (%)
<i>RR = 4.5</i>			
0.7	7.85	7.43	4.86
0.8	7.79	7.49	3.47
<i>RR = 4.75</i>			
0.7	8.28	7.37	10.40
0.8	8.09	7.79	3.47

Note: the isobutylene conversion refers to the  $i_{net} / o_{utlet}$  of the reactive distillation column



**Fig. 5** Studied reactive distillation column designs; (a): the original design; (b): one reactive tray added to increase residence time in contact with the catalyst; (c): one reactive tray and 5 mass % distillate recycle added to reduce the temperature difference between the trays in the reactive section



**Fig. 6** Influence of operating and design parameters of the column on the value of the target function; (a): the original design; (b): one reactive tray added; (c): one reactive tray and 5 mass % distillate recycle added demonstrates the results of the study for various structures of the reaction distillation column. During the simulation,

$RR$  used as a specification parameter, while  $QN$ ,  $\varepsilon_{isobut}$  and  $x_{ETBE}$  were calculated in Aspen Plus v.10.1. [30] The optimal  $\Psi$  value was further calculated by Eq. (6).

It is obvious that the addition of reactive tray above the feed tray Fig. 6 (b) and the reflux recycle to the reactive section Fig. 6 (c) can significantly increase the performance of the RD column, since these structures provide minimum values of the target function  $\Psi$  at low heat loads and reflux ratios, which corresponds to optimal operating costs. According to Fig. 6 (c), the optimal region of the  $\Psi$  value corresponds to dark blue zone (circled in red) at minimal  $QN$  and  $RR$ . The optimal point corresponds to the  $\Psi$  value of 0.000436:

$$QN = 12.11 \text{ kW}; RR = 8.10.$$

The design parameter study reveals that for each topology there is a reboiler duty and reflux ratio pair that allows for optimal column operation, as presented in Table 5.

Each pair corresponds to a minimal  $\Psi$  value, and also, represents the minimal energy requirements for the column to operate at such  $\Psi$  value (see Fig. 6).

As such, topological optimization alone can give a reduction of 23% in reboiler heat duty and 32% in reflux ratio (scenario (c) compared to (a) (Table 5)).

The present work is limited to the evaluation of design and operation methods for optimizing the performance of reaction distillation.

Capital and operational costs associated with the process structures studied above are not considered.

**Table 5** Minimal energy requirements

Design	Reboiler duty ( $QN$ (kW))	Reflux ratio ( $RR$ )
(a)	15.90	12.00
(b)	14.70	10.90
(c)	12.11	8.10

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## 5 Conclusion

For the proposed study, the mathematical model of the ETBE synthesis reactive distillation column had been developed in Aspen Plus v.10.1 [30], a target function, which takes into account isobutylene conversion and purity of the main product, had been proposed. The parametric sensitivity of the target function to the operating and design parameters of the column had been studied. The areas of steady states multiplicity were found, the optimal structure of the column was defined, the optimal modes of its operation were determined.

For the studied feed composition and feed rate, the optimal structure of the column should include an additional tray in the reactive section and a recycle of 5 mass % of distillate above the feed tray. The optimal reboiler heat load was 12.11 kW, the optimal reflux ratio was 8.10. The performed studies make it possible to exclude operation in the areas of "undesirable" steady states, to carry out technical and economic analysis and optimization.

## Nomenclature

- $a$ : activity;  
 $G$ : volume flow rate (L/s);  
 $K$ : chemical equilibrium constant;  
 $K_A$ : adsorption constant;  
 $k_r$ : reaction-rate constant (mole  $\text{kg}^{-1} \text{s}^{-1}$ );  
 $m_{cat}$ : mass of the catalyst (kg);  
 $n$ : molar flowrate (mole  $\text{s}^{-1}$ );  
 $P$ : pressure (kPa);  
 $QN$ : reboiler heat load (kW);  
 $R$ : universal gas constant (8.314 J  $\text{mole}^{-1} \text{K}^{-1}$ );  
 $r$ : reaction rate (mole  $\text{s}^{-1}$ );  
 $RR$ : reflux ratio;  
 $T$ : temperature (K);  
 $x$ : purity (mass frac.);  
 $\Delta P$ : pressure drop (kPa);  
 $\varepsilon$ : conversion (mole frac.);  
 $\Psi$ : target function.

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