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Dynamic behaviour of a CSTR with reactive distillation

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Abstract

The primary question concerning the safety analysis of an equipment, in which chemical reactions take place, is the knowledge of the existence of multiple steady states. The presence of this phenomenon reduces equipment operability and controllability, particularly during its start-up. Multiple steady states were found in the reactive distillation (RD) process, for example in methyl tertiary-butyl ether (MTBE) synthesis. Steady-state analysis and dynamic simulation of a MTBE reactive distillation have been done in the present paper. The basic kinetic model of MTBE production was applied for simulation of the process in a CSTR with total condenser. The steady-state behaviour of the system was studied in terms of the input parameters, i.e. feed flow rate of methanol, feed flow rate of hydrocarbons, reflux ratio and heating rate and ratio of hydrocarbons in the feed. The dynamic behaviour of the system during the start-up of the CSTR with total condenser was studied. Different perturbations of the manipulated variables were found to cause transitions between parallel steady states and these were also investigated using dynamic simulations.

Keywords: Reactive distillation; CSTR; MESH model; MTBE; Steady states analysis; Dynamic analysis; Multiple steady states; Safety analysis

1. Introduction

The technology of integrating reactors with separators has made a significant progress in the last decade. These processes have often a better conversion and selectivity and lower capital and operating costs than the corresponding reactor-followed-by-separation technology. For this reason, several processes involving reactive distillation (RD) columns have commercial applications [1].

The benefits of RD are clear and can be summarized as follows [2]:

(a) Simplification or elimination of the separation system can lead to significant capital savings.
(b) Improved conversion of reactant approaching 100%. This increase in conversion gives a benefit in reduced recycle costs.
(c) Improved selectivity. Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagents can lead to reduction of the rates of side reactions and hence improved selectivity for the desired products.
(d) Significantly reduced catalyst requirement for the same degree of conversion.
(e) Avoidance of azeotropes. RD is particularly advantageous when the reactor product is a mixture of species that can form several azeotropes with each other. RD conditions can allow the azeotropes to be "reacted away" in a single vessel.
(f) Reduced by-product formation.
(g) Heat integration benefits. If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporisation and reduce the reboiler duty.
(h) Avoidance of hot spots and runaways using liquid vaporisation as thermal flywheel.

A well-known example of this sort of processes is the production of MTBE, or more ecological substances, for example ethyl-tertiary butyl ether (ETBE).

Reactive distillation processes may display a variety of dynamic phenomena, however in the reactive distillation of MTBE, various researches have focused their attention on multiple steady states [1–7].

The multiplicity may have severe safety consequences, but more commonly technological problems, for example lower

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Nomenclature

a	activity
A_1, A_2, A_3, A_4, A_5 and A_6	parameters in Eq. (13)
c_{L}	ion-exchange capacity to the catalyst volume (eq(H$^{\oplus}$) l^{-1})
E	activation energy (J mol^{-1})
F	feed stream (mol s^{-1})
H	molar enthalpy (J mol^{-1})
$\Delta_r H$	heat of reaction (J mol^{-1})
k	reaction rate constant (mol s^{-1} eq^{-1})
K_{a}	reaction equilibrium constant
K_i	vapour–liquid equilibrium constant for component i
L	liquid flow rate (mol s^{-1})
N_{F}	number of feed streams
N_{I}	number of components
N_{R}	number of reactions
P	pressure of the system (Pa)
P_i^0	vapour pressure of pure component i (Pa)
Q	heating rate (J s^{-1})
r	reaction rate (mol m^{-3} s^{-1})
R	gas constant (J mol^{-1} K^{-1})
R_x	reflux ratio
t	time (s)
T	temperature of the system (K)
U	molar hold-up (mol)
V	vapour flow rate (mol s^{-1})
V_{c}	volume of the catalyst (m^3)
V_{r}	volume of the liquid phase in the reactor (m^3)
x	mole fraction in the liquid phase
y	mole fraction in the vapour phase

Greek letters

β	parameter defined by Eq. (14)
γ	activity coefficient
ν	stoichiometric coefficient
ρ	molar density (mol m^{-3})

Superscripts

o	initial conditions

Subscripts

*	Eq. (12) (at temperature $T_* = 333$ K)
**	Eq. (13) (at temperature $T_{**} = 298.15$ K)
C4	C4-fraction (=isobutene + 1-butene)
CSTR	continuous stirred tank reactor
ETBE	ethyl-tertiary butyl ether
f	feed stream index
i	component index
IB	isobutene
INERT	inert components (1-butene)
j	reaction index
L	referring to the liquid phase
MeOH	methanol
MTBE	methyl-tertiary butyl ether
TC	referring to the total condenser
V	referring to the vapour phase

conversion or lower purity of products, which are connected with the existence of multiple steady states.

Mohl et al. [3] discussed that the multiplicity found for a reactive distillation column has the same source as the multiplicity found for the continuous stirred tank reactor. For this reason, the one-stage column consisting of a partial reboiler and a total condenser was studied in their paper. Our attention is also aimed at a CSTR with total condenser. In the present paper, the steady-state behaviour of MTBE processes was studied in terms of the input parameters feed, like flow rate of methanol, feed flow rate of hydrocarbons, reflux ratio and heating rate and ratio of hydrocarbons in the feed stream. To describe the dynamics of a CSTR with total condenser, an equilibrium (EQ) mathematical model was developed. Different perturbations of the variables were investigated to cause transitions between parallel steady states and these were also simulated.

The determination and investigation of the existence of multiple steady states is often a very complicated process. The professional integrated simulation software HYSYS is not able to solve the reactive distillation problems, where multiple steady states occur [7]. In our case, the multiple steady states were determined by the CONT software presented in ref. [8]. CONT was integrated in our program, which is able to simulate the steady state and dynamic behaviour of a CSTR with total condenser.

2. Theoretical

2.1. Mathematical model

MESH equations (**M**aterial balances, vapour–liquid **E**quilibrium equations, mole fraction **S**ummations and enthalpy (**H**) balances) [2], equations for the molar hold-up in the CSTR and kinetic equations are used as the basic equations for the model of a CSTR with total condenser (see Fig. 1).

A mathematical model presented below was developed under following assumptions:

- ideal phase equilibrium in the reactor (i.e. vapour–liquid equilibrium is attained),
- vapour and liquid in the reactor and leaving the reactor are perfectly mixed and the liquid in the reactor has a concentration equal to that of the liquid leaving the reactor,
- reversible reactions proceed only in the liquid phase and their course can be described by appropriate kinetic equations,
- constant volumetric hold-up in the CSTR,
- the hold-up per CSTR is equal to the liquid hold-up in the CSTR (the molar vapour hold-up is negligible compared to the molar liquid hold-up),
- the molar hold-up in the total condenser is negligible,
- no reaction proceeds in the total condenser,

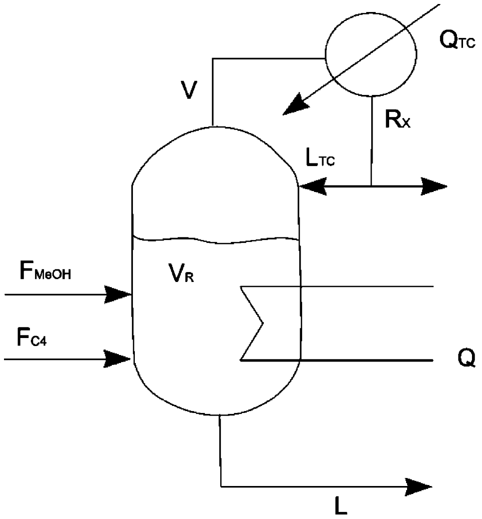

Fig. 1. Schematic diagram of the CSTR with total condenser.

- the reflux from the total condenser is returned back to the CSTR at condensation temperature.

2.2. Model equations

M equations are the material balance equations; the total material balance takes the form:

$$\frac{\mathrm{d}U}{\mathrm{d}t} = \sum_{f=1}^{N_\mathrm{F}} F_f + V_\mathrm{c}\sum_{j=1}^{N_\mathrm{R}}\left(r_j\sum_{i=1}^{N_\mathrm{I}}\nu_{j,i}\right) + L_\mathrm{TC} - V - L \tag{1}$$

The component mass balance (neglecting the vapour hold-up) is

$$\frac{\mathrm{d}(Ux_i)}{\mathrm{d}t} = \sum_{f=1}^{N_\mathrm{F}} F_f x_{f,i} + V_\mathrm{c}\sum_{j=1}^{N_\mathrm{R}}(r_j\nu_{j,i}) + L_\mathrm{TC}x_{\mathrm{TC},i} - Vy_i - Lx_i \tag{2}$$

The enthalpy (**H**) balance is given by

$$\frac{\mathrm{d}(UH_\mathrm{L})}{\mathrm{d}t} = \sum_{f=1}^{N_\mathrm{F}} F_f H_f + V_\mathrm{c}\sum_{j=1}^{N_\mathrm{R}} r_j(-\Delta_r H_j) + L_\mathrm{TC}H_\mathrm{TC} - VH_\mathrm{V} - LH_\mathrm{L} + Q \tag{3}$$

The **S** equations are the summation equations

$$\sum_{i=1}^{N_\mathrm{I}} x_i = 1, \quad \sum_{i=1}^{N_\mathrm{I}} y_i = 1 \tag{4}$$

The **E** equations are the phase equilibrium relations

$$y_i = K_i x_i \tag{5}$$

The reflux rate from the total condenser to the CSTR (L_TC) is

$$L_\mathrm{TC} = V\frac{R_x}{R_x + 1} \tag{6}$$

The total molar hold-up (U) is given by:

$$U = \frac{V_\mathrm{r}}{\sum_{i=1}^{N_\mathrm{I}} x_i/\rho_i} \tag{7}$$

After all assumptions for the total condenser, there is only one unknown parameter. This parameter is the temperature of the condensate (condensation temperature) given by the following equation:

$$P = \sum_{i=1}^{N_\mathrm{I}} P_i^\mathrm{o} x_{\mathrm{TC},i}\gamma_i \tag{8}$$

This system of differential and algebraic equations (Eqs. (1)–(8)) was solved for actual initial conditions, which are defined as follows:

$$t = 0:\ x_i = x_i^0,\ y_i = y_i^0,\ T = T^0,\ U = U^0,\ V = V^0,\ L = L^0 \quad \text{and}\ T_\mathrm{TC} = T_\mathrm{TC}^0 \tag{9}$$

2.3. Computational methods

The mathematical model presented above, consists of a set of ordinary differential and algebraic equations. Differential equations are obtained from mass and energy balances of the CSTR. The algebraic equations describe the particular variables and physical properties [9]. In the steady state, equations of the MESH model form a set of nonlinear algebraic equations.

- Steady state—Fortran subroutine to solve a system of nonlinear equations using a modified Powel hybrid algorithm and a finite-difference approximation to the Jacobian.
- Identification of multiple steady states continuation algorithm, which is a modification of the CONT software presented in ref. [8].
- Dynamic simulation—Fortran subroutine to solve a system of differential/algebraic equations [10].

3. Case study—production of MTBE

3.1. Reaction system

MTBE is produced according to the following reaction scheme:

$$CH_3OH + (CH_3)_2C{=}CH_2 \Leftrightarrow (CH_3)_3COCH_3 \tag{R1}$$

where isobutene (IB) reacts with methanol (MeOH) to form MTBE in a reversible exothermic reaction. The reaction is catalyzed by strong catalytic ion-exchange resins. The reaction rate is given by [11]:

$$r = k\left(\frac{a_\mathrm{IB}}{a_\mathrm{MeOH}} - \frac{1}{K_\mathrm{a}}\frac{a_\mathrm{MTBE}}{a_\mathrm{MeOH}^2}\right)c_\mathrm{L} \tag{10}$$

$$a_\mathrm{i} = \gamma_\mathrm{i}(T, P, x_\mathrm{i})x_\mathrm{i} \tag{11}$$

The temperature dependence of the rate constant is defined by the Arrhenius equation,

$$k = k(T_*)\exp\left[-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_*}\right)\right] \tag{12}$$

where $k(T_*)$ is the rate constant at temperature T_*.

The temperature dependence of the equilibrium constant is given, for example by [11]:

$$\ln\left[\frac{K_a(T)}{K_a(T_{**})}\right] = A_1\left(\frac{1}{T}-\frac{1}{T_{**}}\right) + A_2\ln\frac{T}{T_{**}} + A_3(T-T_{**}) + A_4(T^2-T_{**}^2) + A_5(T^3-T_{**}^3) + A_6(T^4-T_{**}^4) \tag{13}$$

where K_a (T_{**}) is the equilibrium constant at temperature T_{**} and $A_1 = -1.49277\times10^3$ K, $A_2 = -7.74002\times10^1$, $A_3 = 5.07563\times10^{-1}\,K^{-1}$, $A_4 = -9.12739\times10^{-4}\,K^{-2}$, $A_5 = 1.10649\times10^{-6}\,K^{-3}$ and $A_6 = -6.27996\times10^{-10}\,\mathrm{K}^{-4}$.

The parameters for the temperature dependence of the reaction rate r, the reaction rate constant k and the temperature dependence of the equilibrium constant K_a are defined in ref. [11] or refs. [6,12,13] (see Table 1). The reaction is usually carried out in the presence of inert components. These inert components result from upstream processing, where isobutene is produced. For MTBE synthesis 1-butene is used as inert [7].

3.2. Operation conditions

Methanol and hydrocarbons were fed into a CSTR as two separate streams. The inflow temperature of both streams was 320 K and the system pressure was 1110 kPa. At standard operating conditions, the molar flow rate of methanol was 533.6 kmol h^{-1} and the molar flow rate of hydrocarbons was 1976.4 kmol h^{-1}. The reflux ratio was set to 10 and the heating rate was 1.56×10^7 kJ h^{-1}. The volume of the liquid phase in the reactor was 5 m^3 and the catalyst volume was 1.5 m^3.

The ratio of reactive hydrocarbons in the feed β, defined as

$$\beta = \frac{x_{\mathrm{f,IB}}}{x_{\mathrm{f,IB}} + x_{\mathrm{f,INERT}}} \tag{14}$$

was set to 0.45.

The vapour–liquid equilibrium for the MTBE process was calculated using the Wilson model with the binary interaction parameters given in HYSYS 2.1 (see Table 2). The gas phase was supposed to be ideal.

Table 1
Model parameter for Eqs. (10)–(13)

Parameter	Unit	Value
k (333 K)	mmol s^{-1} eq^{-1}	15.5
E	kJ mol^{-1}	92.4
K_a (298.15 K)		300.5
c_L	eq(H$^{\oplus}$) l^{-1}	0.9

Table 2
Binary interaction parameters for Wilson equations

	Methanol	Isobutene	MTBE	1-Butene
Methanol	0.0	920.5302	−1192.3647	753.6095
Isobutene	8490.9343	0.0	873.6694	176.0920
MTBE	4647.4366	−84.6256	0.0	−117.5160
1-Butene	8682.9924	−128.448	889.9117	0.0

4. Results and discussion

4.1. Steady-state behaviour

The locus of multiple steady states was performed by the continuation algorithm, which is a modification of the CONT software presented by refs. [8,14,15]. The steady-state behaviour of the MTBE processes was studied in terms of the input parameters, i.e. feed flow rate of MeOH, feed flow rate of IB, reflux ratio R_x, heating rate Q and ratio of hydrocarbons in the feed β. For different constant values of

(a) the reflux ratio R_x (Fig. 2),
(b) the heating rate Q (Fig. 3),
(c) ratio of hydrocarbons in the feed β (Fig. 4),

the MeOH feed flow rate was used as a continuation parameter.

These solution diagrams give some information relevant for process design and operation of the MTBE synthesis. A distinct maximum of MeOH conversion for different values of investigated parameters (R_x, Q, β) was observed.

For different values of investigated parameters (R_x, Q, β), different ranges of MeOH feed flow rates with multiple regions exist. The smaller the reflux ratio R_x, the smaller is the region of MeOH feed flow rates, where multiple steady states occur (Fig. 2). Another influence on the extent of the multiplicity region has the heating rate Q. In this case (Fig. 3), a smaller amount of heating rate Q causes a larger region of multiple steady

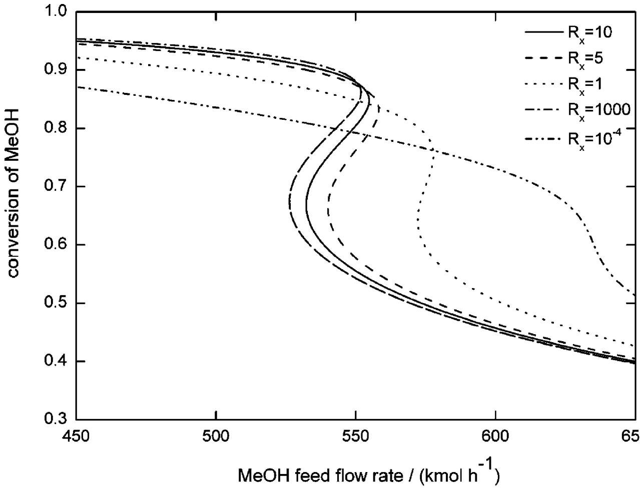

Fig. 2. Solution diagram of MeOH conversion as a function of the MeOH feed flow rate for different reflux ratios R_x ($Q = 1.56\times10^7$ kJ h^{-1}, $\beta = 0.45$).

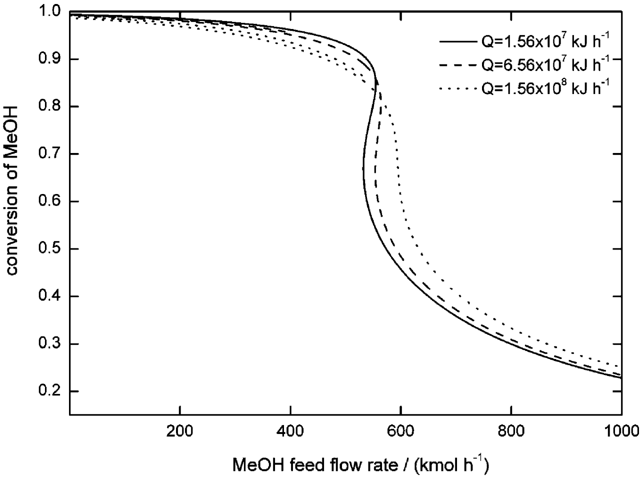

Fig. 3. Solution diagram of MeOH conversion as a function of the MeOH feed flow rate for different heating rates Q ($R_x = 10$, $\beta = 0.45$).

states. The bifurcation diagram for different ratios of hydrocarbons in the feed β (Fig. 4) indicates that the extension of the multiple steady states region is not changed by this ratio. However, a movement of location of the multiple steady states may be observed.

4.2. Dynamic behaviour

4.2.1. Start-up of the reactor

The presence of multiple steady states reduces equipment operability and controllability, particularly during the start-up to the desired operating point. The bifurcation diagram (Fig. 5), where the C4 feed flow rate was used as a continuation parameter and the other operation parameters were assumed to be constant ($R_x = 10$, $Q = 1.56 \times 10^7\,\text{kJ h}^{-1}$, $\beta = 0.45$ and $F_{\text{MeOH}} = 533.6\,\text{kmol h}^{-1}$), indicated three steady states (stable steady state, white circle; unstable steady state, black circle) at the operating value of the C4 feed flow rate ($1976.4\,\text{kmol h}^{-1}$).

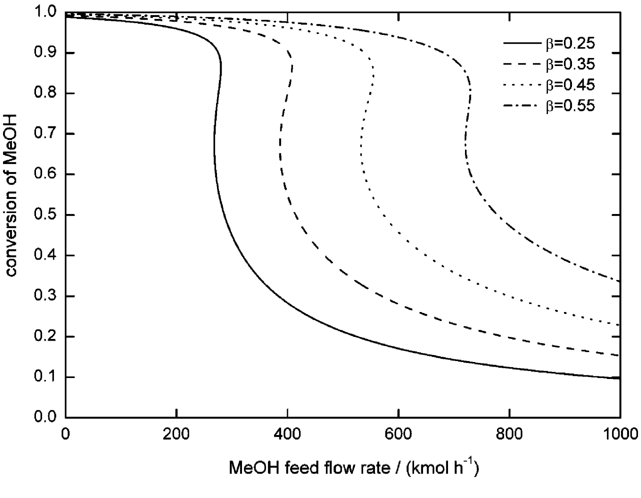

Fig. 4. Solution diagram of MeOH conversion as a function of the MeOH feed flow rate for different ratios of hydrocarbons in the feed β ($R_x = 10$, $Q = 1.56 \times 10^7\,\text{kJ h}^{-1}$).

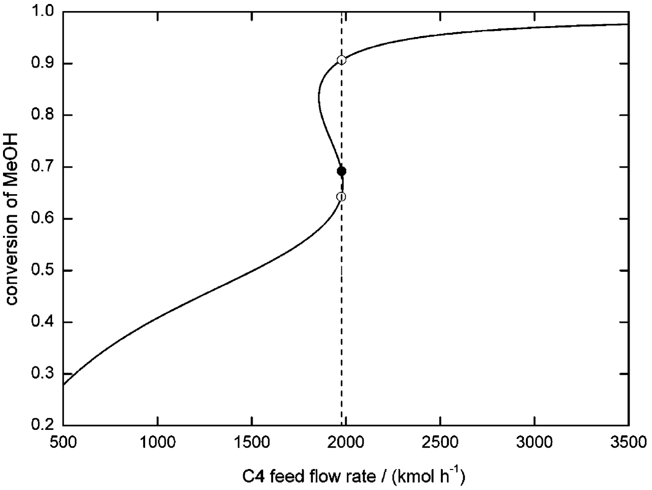

Fig. 5. Solution diagram of MeOH conversion, where the C4 feed flow rate was used as a continuation parameter.

Two ways of the start-up procedure were simulated. The start-up procedure of the CSTR with total condenser was initiated by:

(a) gradual increase in the C4 feed flow rate,
(b) gradual increase in the MeOH feed flow rate.

Prior to the start-up procedure by an increase in the C4 feed flow rate to the reactor, the reactor was charged with pure methanol. Prior to the start-up procedure by an increase in the MeOH feed flow rate, the reactor was charged mainly with the C4 feed flow stream containing a small amount of MeOH.

The start-up of the CSTR (previously charged with pure MeOH) by a gradual increase in the C4 feed flow rate up to the operating value of $1976.4\,\text{kmol h}^{-1}$ is shown in Fig. 6. The reactor is stabilized to the lower steady state characterized by the temperature of 356.7 K and a lower conversion of MeOH (63.65%).

The start-up of the CSTR by an increase in the C4 feed flow rate to a higher steady state is possible, if the C4 feed flow rate increases to a value higher than the operating rate and then decreases to a normal operating value of $1976.4\,\text{kmol h}^{-1}$

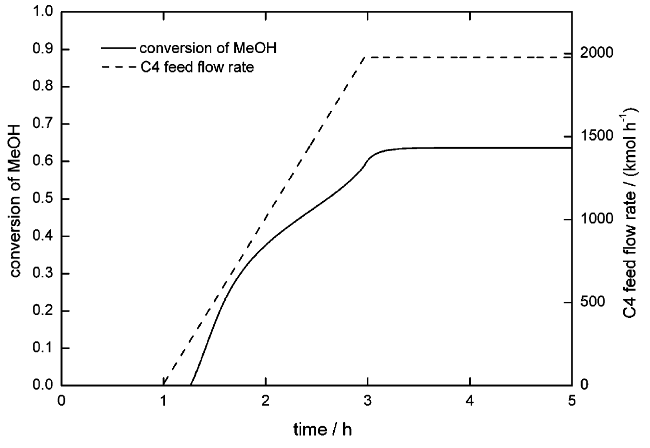

Fig. 6. Start-up of the CSTR with total condenser by an increase in the C4 feed flow rate to lower steady state.

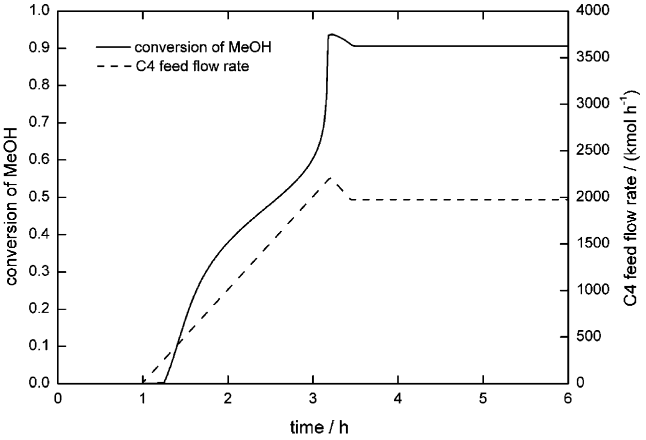

Fig. 7. Start-up of the CSTR by an increase of the C4 feed flow rate to higher steady state.

(Fig. 7). After the conversion of MeOH reached the multiple steady state region, it was switched to the stable higher branch. When the C4 feed flow rate was again equal to the operating value, the conversion was stabilized to higher steady state. This stable steady state is characterized by the temperature of 360.8 K and a higher conversion of MeOH (90.65%).

The start-up of the CSTR (previously charged with C4) by a gradual increase in the MeOH feed flow rate to the operating value of 533.6 kmol h^{-1} is shown in Fig. 8. In this case, the reactor is switched to the higher steady state immediately after the operating value of the MeOH feed flow rate was reached. This dynamic "way" was indicated by the bifurcation diagram depicted in Fig. 2.

4.2.2. Transition between steady states

In addition, the dynamic behaviour of the system with disturbances of the inlet stream of the C4 feed flow stream was studied. The initial conditions were considered to be "normal" operating conditions. At time equal to 1 h, a very fast decrease in the C4 feed flow rate was simulated, and after 0.5 h the original flow rate of C4 was reached. At first, the decrease of the C4 feed flow rate was to 1880 kmol h^{-1} (Fig. 9). After returning the C4 feed flow rate to the operating value, the CSTR works again in the higher original steady state. However, if the decrease in the C4 feed flow rate was 1700 kmol h^{-1} (Fig. 10), the system was stabilized to a different stable steady state as before the perturbation (lower steady state). The "ways" of transition between the steady states are plotted in Fig. 11.

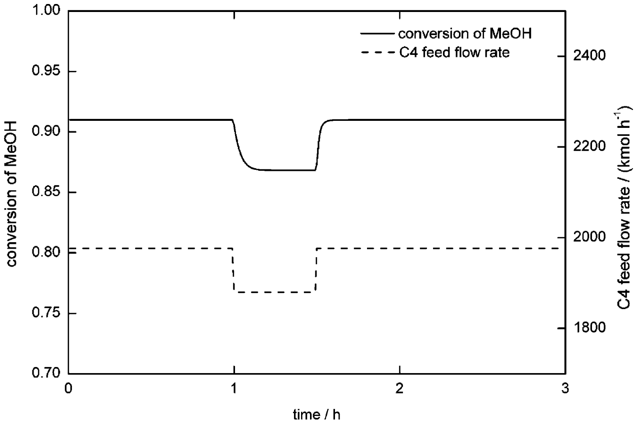

Fig. 9. Step change of the C4 feed flow rate from the value of 1976.4–1880 kmol h^{-1} and back.

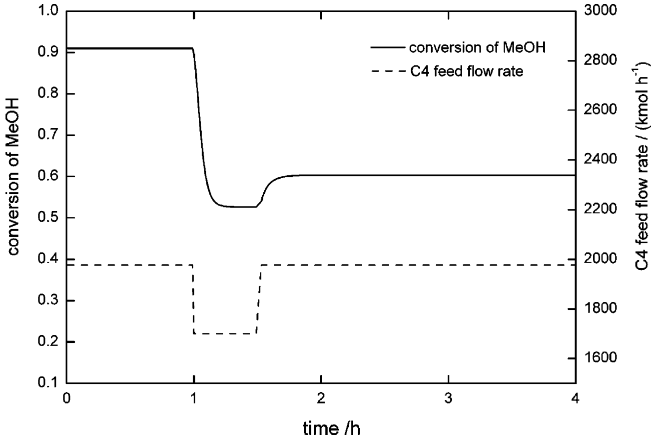

Fig. 10. Step change of the C4 feed flow rate from the value of 1976.4–1700 kmol h^{-1} and back.

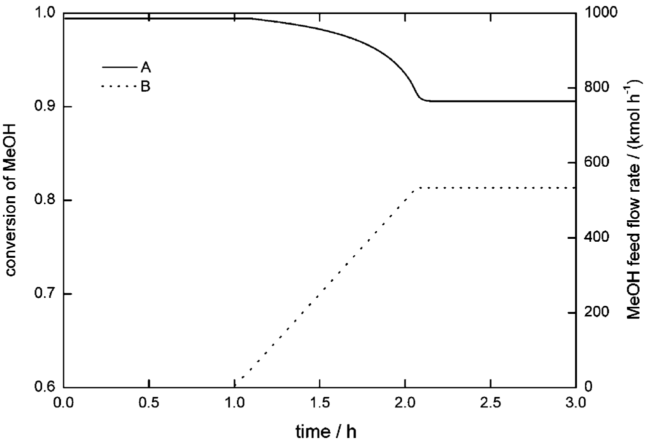

Fig. 8. Start-up of the CSTR by an increase in the MeOH feed flow rate to higher steady state.

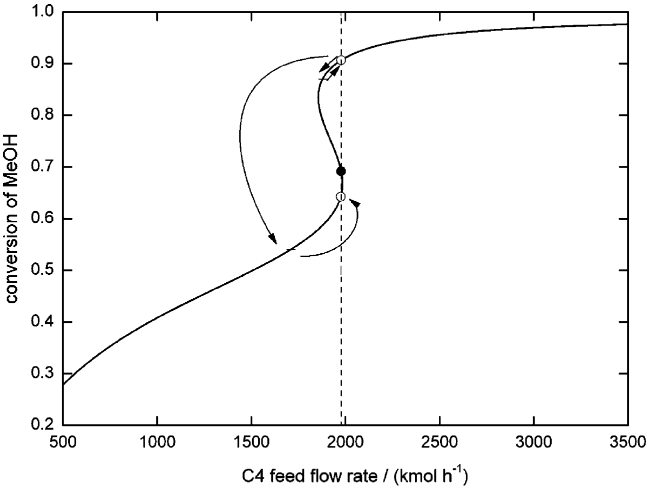

Fig. 11. The "ways" of transition between steady states.

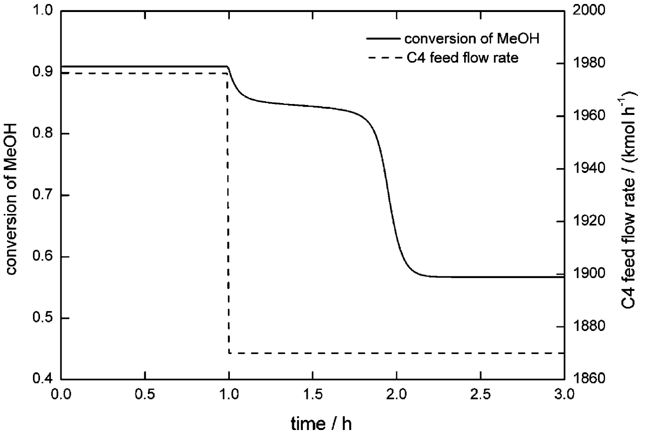

Fig. 12. Step change of the C4 feed flow rate from the value of 1976.4–1870 kmol h^{-1}.

If the step change in the flow rate is so extensive, that the reactor is shifted to the steady state on the lower stable branch, after the return of the feed flow rate to the operating value of 1976.4 kmol h^{-1}, the CSTR is always shifted to the steady state, which is on this lower branch.

The dynamic behaviour of the system during changes of the C4 feed flow rate was also studied. If a step change of the C4 feed flow rate occurs, the CSTR with total condenser is forced to find a new steady state. We investigated the step change of the C4 feed flow rate from the value of 1976.4–1870 kmol h^{-1} (Fig. 12). The CSTR with total condenser is shifted to a lower stable steady state. These stable steady states can be found in the solutions diagrams (see Fig. 5).

In the case study, a gradual decrease in the C4 feed flow rate was also studied. At time equal to 1 h a very slow gradual decrease in the C4 feed flow rate was simulated and after 3.78 h the flow rate of C4 of 1700 kmol h^{-1} was reached (Fig. 13). At first, the CSTR with total condenser follows the stable branch. At time equal to about 2 h, the conversion falls down on the lower stable branch and follows this branch until the C4 feed flow rate of 1700 kmol h^{-1} is reached. This dynamic "way" was indicated by the bifurcation diagram depicted in Fig. 5.

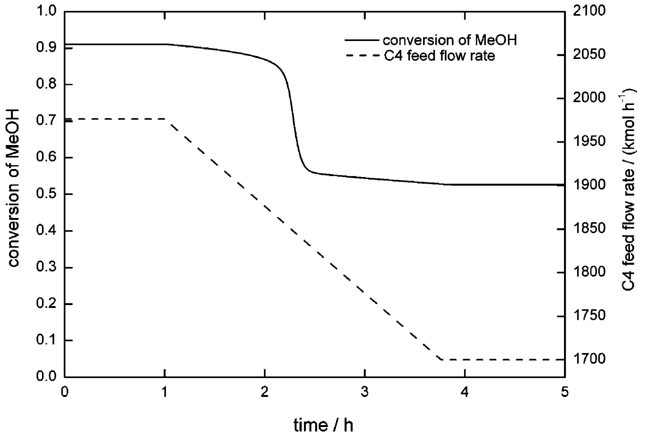

Fig. 13. Gradual change of the C4 feed flow rate from the value of 1976.4–1700 kmol h^{-1}.

5. Conclusions

A dynamic simulation model of reactive distillation of MTBE in a CSTR with total condenser was developed to study the effect of various disturbances of the system's operating conditions. After some assumptions, the mathematical equilibrium model (MESH model) was used.

Multiple steady states were found and investigated for different input parameters, i.e. feed flow rate of MeOH, feed flow rate of IB, reflux ratio R_x, heating rate Q and ratio of hydrocarbons in the β. A movement of the multiple steady states region was observed in the dependence of the input parameters.

It was shown that the multiplicity of steady states complicates the start-up procedure of the operating point from different initial conditions. During the start-up of the CSTR by an increase in the C4 feed flow rate to the operating value, the reactor is switched to the lower stable steady state. The start-up to the higher stable steady state has been possible by a gradual increase in the MeOH feed flow rate to the operating value or if an increase in the C4 feed flow rate is above the operating value with a consecutive decrease in the C4 feed flow rate to the operating value.

Disturbances of the input parameter – the C4 feed flow rate – were investigated to produce transitions between the parallel steady states, or to shift the CSTR with total condenser to another stable steady state. It was shown that the bifurcation diagram can solidly predict the behaviour of the system during dynamic simulations.

It is important to point out that the multiplicity found for reactive distillation is connected with safety consequences, but more commonly with technological problems, in the same way as the multiplicity found for the continuous stirred tank reactor.

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References

[1] S. Schrans, S. de Wolf, R. Baur, Dynamic simulation of reactive distillation: an MTBE case study, Comput. Chem. Eng. 20 (Suppl. 2) (1996) S1619–S1624.

[2] R. Taylor, R. Krishna, Modelling reactive distillation, Chem. Eng. Sci. 55 (22) (2000) 5183–5229.

[3] K.-D. Mohl, A. Kienle, E.-D. Grilles, P. Rapmund, K. Sundmacher, U. Hoffmann, Steady-state multiplicities in reactive distillation columns for the production of fuel ethers MTBE and TAME: theoretical analysis and experimental verification, Chem. Eng. Sci. 54 (8) (1999) 1029–1043.

[4] A.P. Higler, R. Taylor, R. Krishna, Nonequilibrium modelling of reactive distillation: multiple steady states in MTBE synthesis, Chem. Eng. Sci. 54 (10) (1999) 1389–1395.

[5] M.G. Sneesby, M.O. Tade, T.N. Smith, Steady-state transitions in the reactive distillation of MTBE, Comput. Chem. Eng. 22 (7–8) (1998) 879–892.

[6] C. Thiel, K. Sundmacher, U. Hoffmann, Residue curve maps for heterogeneously catalysed reactive distillation of fuel ethers MTBE and TAME, Chem. Eng. Sci. 52 (6) (1997) 993–1005.

[7] M. Šoóš, J. Markoš, Ľ. Jelemenský, Safety of chemical reactors, Pet. Coal 43 (3–4) (2001).

[8] M. Marek, I. Schreiber, Chaotic Behaviour of Deterministic Dissipative Systems, Academia Praha, Praha, 1991.

[9] K. Alejski, F. Duprat, Dynamic simulation of the multicomponent reactive distillation, Chem. Eng. Sci. 51 (18) (1996) 4237–4252.

[10] L.R Petzold, P.N. Brown, A.C. Hindmarsh, C.W. Ulnch.ode/daskr.tgz, http://netlib3.cs.utk.edu/cgi-bin/search.pl?query=gams/I1a2%2A.

[11] A. Rehfinger, U. Hoffmann, Kinetics of methyl tertiary butyl ether liquid phase synthesis catalyzed by ion exchange resin. I. Intrinsic rate expression in liquid phase activities, Chem. Eng. Sci. 45 (6) (1990) 1605–1617.

[12] K. Sundmacher, U. Hoffmann, Macrokinetic analysis of MTBE-synthesis in chemical potentials, Chem. Eng. Sci. 49 (18) (1994) 3077–3089.

[13] K. Sundmacher, G. Uhde, U. Hoffmann, Multiple reactions in catalytic distillation processes for the production of the fuel oxygenates MTBE and TAME: analysis by rigorous model and experimental validation, Chem. Eng. Sci. 54 (13–14) (1999) 2839–2847.

[14] M. Holodniok, A. Klič, M. Kubíček, M. Marek, Methods of Analysis of Nonlinear Dynamic Models, Academia Praha, Praha, 1986.

[15] M. Kubíček, Algorithm 502. Dependence of solution of nonlinear systems on a parameter [C5], ACM Trans. Math. Software 2 (1) (1976) 98–107.