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Impact of mathematical model selection on prediction of steady state and dynamic behaviour of a reactive distillation column

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ABSTRACT

The objective of this paper was to compare the prediction of the equilibrium (EQ) and nonequilibrium (NEQ) models during safety analysis of a reactive distillation column focusing on the identification of hazardous situations or particular operability problems. The safety and operability analyses are based on application of the HAZOP procedure integrated with a mathematical model with the aim to determine the column response to deviations from normal operation conditions or during a nonstandard procedure, e.g. the start-up of the reactive distillation column. A significant part of the safety and operability problems analysis is the identification of multiple steady states and their stability. A reactive distillation column can in general exhibit multiple steady states which reduce the column operability and controllability during perturbations of the manipulated variables and particularly during the start-up and shut down procedures. The EQ and NEQ models were compared focusing on prediction of the multiple steady states phenomenon and of the consequences which can result from this phenomenon.

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1. Introduction

Identification of possible steady states and a detailed dynamic simulation of operational failures of a reactive distillation column have led to a deeper understanding of the process behaviour and its proper design. Using an adequate mathematical model, risks can be assessed for normal operation states as well as for case of operational failures (Can, Jimoh, Steinbach, & Wozny, 2002). Mathematical model of a reactive distillation column integrated with a hazard identification method could be a very useful tool for safety analysis not only of a working apparatus (reactive distillation column), but also in all steps of its design. There are several methods for hazard identification in chemical industry: screening—index methods, Checklists method, What if? Analysis, FMECA (Failure Mode, Effect and Criticality Analysis), HAZOP, etc. (Lees, 1996). HAZOP is one of the best and most rigorous techniques for identification of hazard and operability problems in a chemical plant (Kletz, 1999). The HAZOP procedure formally examines all equipment step by step as well as deviations from its normal operation conditions and considers what failures can occur. The HAZOP report includes all the deviations, their causes, consequences in the equipment performance, analysis of these consequences, implemented protection (active and/or passive), and the resulting suggestions. In the last 20 years, a lot of research efforts has been dedicated to the development of intelligent systems for automated HAZOP analysis (Shimada, Suzuki, & Sayama, 1996; Weatherill & Cameron, 1989). The main advantages of this approach are:

(1) significantly reducing the time and effort required in HAZOP;
(2) making the study more smooth and detailed;
(3) minimising the influence of human factors.

Usually, the HAZOP analysis does not consider the duration and amplitude of the deviations generated during the operation. However, what exactly does the deviation 'less flow' mean: 90% or 20% of the usual operation value? Does the deviation occur as an immediate (step) decrease of the flow lasting ten or more minutes, or is it only an impulse? Is this decrease continuous at some rate? Answers to these questions can be obtained using an appropriate mathematical model. In such a model, the extent of the deviations can be easily incorporated and possible consequences investigated (Labovský, Jelemenský, & Markoš, 2006; Švandová, Markoš, & Jelemenský, 2005).

A significant part of the safety analysis of a reactive distillation column (as well as of various types of chemical reactors) (Molnár, Markoš, & Jelemenský, 2005) is the steady state analysis, which includes the identification of multiple steady states and their stability. Taylor and Krishna (2000) reported that the combination of distillative separation with a chemical reaction leads to a complex interaction between the vapour–liquid equilibrium, vapour–liquid

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mass transfer, intra-catalyst diffusion (for heterogeneously catalysed processes) and chemical kinetics. Such interactions lead to a possible existence of multiple steady states, which has been verified in experimental laboratory and pilot plant units (Mohl et al., 1999; Rapmund, Sundmacher, & Hoffmann, 1998). The existence of multiple steady states can result in dangerous situations, although more frequently in technological problems, e.g. lower conversion or lower purity of the products. A very characteristic type of multiple steady states are isolated branches of solutions, also called isolas. The first example of an isola in a reactive distillation column was reported by Chen, Huss, Doherty, and Malone (2002).

A reliable prediction of the reactive distillation column behaviour during the safety analysis as well as identification of multiple steady states is influenced by the complexity of the mathematical model which is used for its description. For modelling reactive distillation columns, two distinctly different approaches are available in literature (Baur, Higler, Taylor, & Krishna, 2000; Kooijman & Taylor, 2000; Noeres, Kenig, & Gorak, 2003; Taylor & Krishna, 1993; Taylor & Krishna, 2000): the equilibrium (EQ) stage model in which the vapour and liquid phases are assumed to be in thermodynamical equilibrium and the nonequilibrium (NEQ) stage model in which the finite mass transfer rates across the vapour–liquid interface are accounted for.

The objective of this paper was to compare the prediction of the equilibrium and nonequilibrium models during safety analysis of a reactive distillation column focusing on the identification of hazardous situations or operability problems. The safety and operability analyses are based on application of the HAZOP procedure integrated with a mathematical model with the aim to determine the column response to deviations from normal operation conditions or during a nonstandard procedure, like the start-up of the reactive distillation column.

2. Paper approach

2.1. Mathematical models and computational methods

The basic assumption of the equilibrium model is the equilibrium between the streams leaving the column tray. In equilibrium models, the balance equations are written around the stage as a whole and the composition of the leaving streams related through the assumption that they are in equilibrium or by use of an efficiency equation. The equations describing the equilibrium model are: component Material balances, equations of phase Equilibrium, Summation equations and Heat balance for each stage (MESH equations). The nonequilibrium model of reactive distillation follows the philosophy of rate based models for conventional distillation (Krishnamurthy & Taylor, 1985a,b). The description of the interphase mass transfer is almost invariably based on the Maxwell–Stefan theory for calculation of the interphase heat and mass transfer rates (Kooijman & Taylor, 2000; Krishna & Wesselingh, 1997; Taylor & Krishna, 1993). In a nonequilibrium model, separate material and energy balance equations are written for each phase. These balance equations are linked by material and energy balances around the interface. The equilibrium relations are used to relate the compositions on each side of the phase interface. The interface composition and temperature must, therefore, be determined as part of a nonequilibrium column simulation. The equations describing the nonequilibrium model are: Material balances, Energy balances, Rate equations, Summation equations, eQuilibrium relations for each stage and Hydraulic equations. This system of equations is known as the MERSHQ equations.

Both, the EQ and NEQ models consist of a set of ordinary differential and algebraic equations which were solved by our own FORTRAN code, using:

- for steady state simulation—Fortran subroutine from the IMSL library to solve a system of nonlinear equations using a modified Powel hybrid algorithm and a finite-difference approximation to the Jacobian,
- for identification of multiple steady states – CONT – Continuation and Stability Analysis Package (Kubíček, 1976; Kubíček & Marek, 1983; Marek & Schreiber, 1991),
- for dynamic simulation—Fortran subroutine to solve a system of differential/algebraic equations DDASKR (Petzold, Brown, Hindmarsh, & Ulrich, 2002).

2.2. MTBE case study

As a model system, the MTBE reaction system was chosen:

$$CH_3OH + (CH_3)_2C{=}CH_2 \Leftrightarrow (CH_3)_3COCH_3 \qquad (A)$$

where *iso*-butene (IB) reacts with methanol (MeOH) to form MTBE in a reversible, exothermic reaction. The reaction is catalysed by a strong ion-exchange resin. The reaction rate equation and its parameters are given by Rehfinger and Hoffmann (1990). Possible side-reactions have been ignored. Reaction rates were calculated assuming a pseudohomogenous model. The reaction is usually carried out in the presence of inert components. These inert components result from upstream processing, where *iso*-butene is produced. In our case study, 1-butene was used as an inert. The vapour–liquid equilibrium was calculated using the UNIQUAC model with the binary interaction parameters reported by Rehfinger and Hoffmann (1990) (all binary interactions between MeOH, IB, MTBE) and HYSYS 2.1 (all binary interactions between 1-butene and the other components). Physico-chemical properties of all pure components were taken from the HYSYS 2.1 database.

2.3. Column configuration

The column configuration chosen for the simulations is the configuration described by Jacobs and Krishna (1993) (see Fig. 1). The

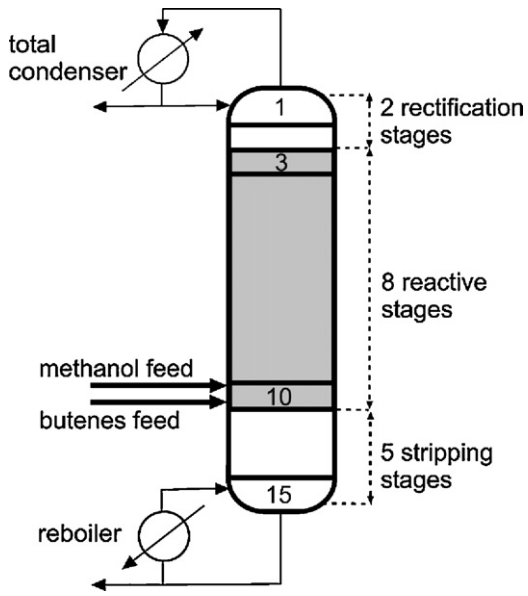

Fig. 1. Reactive distillation column configurations.

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column consisted of a total condenser, 15 sieve trays (2 rectifying stages, 8 reactive stages and 5 stripping stages), and a partial reboiler. On each of the eight stages in the reactive zone, 1000 kg of the catalyst were charged in the form of "envelopes" placed along the flow path length. The details of such a construction are available in a patent (Jones, 1985). The column pressure was 1110 kPa and the column had two feed streams: a methanol feed and a mixed butenes feed, both fed to stage 10. At a standard operating point, the molar flow rates of methanol and the mixture of butenes were 775.8 and 1900 kmol/h, respectively. The reflux ratio was set to 7 and the bottom flow rate to 675 kmol/h. The bottom product consisted predominantly of MTBE. In the EQ model, the stage efficiency of 60% was assumed. This value closely corresponded to the calculations of the NEQ model using the *AICHE* calculation method for sieve tray mass transfer (Baur et al., 2000).

2.4. Results and discussions

During a HAZOP study, possible deviations are generated by rigorous questioning, prompted by a series of standard "guidewords" applied to the intended design (Kletz, 1999). After the guideword is matched with a parameter, a deviation is generated. The next step of a HAZOP study is to look for potential consequences. At this moment, the application of mathematical modelling (steady state analysis and dynamic analysis) is useful in order to find adequate consequences. Steady state solutions over a large interval of operating parameters are obtained by a continuation algorithm. The information about trajectories and conditions able to shift the system from one steady state to another can be obtained by dynamic analysis. With the proposed safety analysis methodology, it is necessary to investigate all deviations of all operating parameters; i.e. temperature, composition, and flow rate of all feed streams into the system and also of the reflux or bottom flow rate, as well as all deviations of their combinations and their consequences. This complex task was, however, out of the range of this paper. Therefore, only the reactants feed flow rate were analysed and discussed here in more detail.

2.4.1. Steady states analysis

The identification of the multiple steady states locus in two-parameter planes (remaining operation parameters were kept constant) was performed using the algorithm CONT (Kubíček, 1976; Kubíček & Marek, 1983; Marek & Schreiber, 1991). The result of these simulations is depicted in Fig. 2, where the methanol feed flow rate and butenes feed flow rate were chosen as the parameters of interest. The bifurcation diagram contains information about the limit points and the multiplicity intervals. White area in this diagram indicates that for the combination of both investigated parameters only one steady state is possible, meanwhile, the filled area represents the three possible steady states for the actual methanol feed flow rate and the actual butenes feed flow rate. The boundary lines of the filled area present the limit points in the investigated parametric plane. Fig. 2 indicates that the multiplicity zones predicted by EQ and NEQ models do not overlap in the whole range of the investigated parameters; however, for the operating methanol feed flow rate (775.8 kmol/h) and the operating butenes feed flow rate (1900 kmol/h), the steady-state multiplicity was predicted assuming both models (black circle in Fig. 2). Fig. 2 provides information about multiplicity intervals; however, it does not give information about conversion in the possible steady states. This information is provided by the solution diagrams (Fig. 3A and B).

In the solution diagrams, either the methanol feed flow rate (with constant butenes feed flow rate set to the value of 1900 kmol/h) or the butenes feed flow rate (with constant methanol feed flow rate set to the value of 775.8 kmol/h) were considered as continuation parameters. The solution diagrams (Fig. 3A), where the methanol feed flow rate was used as a continuation parameter, indicated three steady states at the operating value of the methanol feed flow rate (775.8 kmol h^{-1}) for both models. These curves of the *iso*-butene conversion are continuous. The bifurcation diagram (Fig. 3B.), with the butenes feed flow rate used as a continuation parameter, indicated the same three steady states for both models used at the operating value of the butenes feed flow rate (1900 kmol/h) as those in Fig. 3A. However, very interesting results of these continuations are continuous curves of the

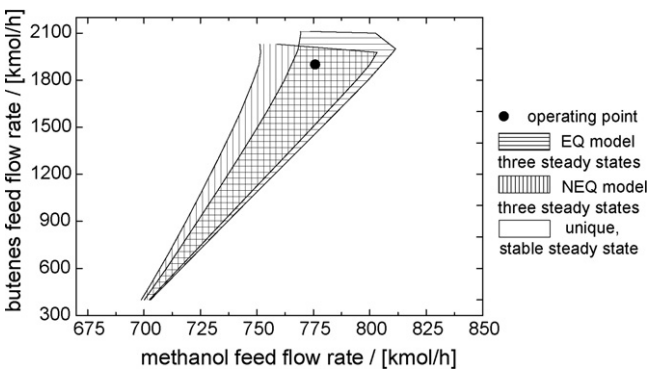

Fig. 2. Bifurcation diagram in the parametric plane methanol feed flow rate and butenes feed flow rate.

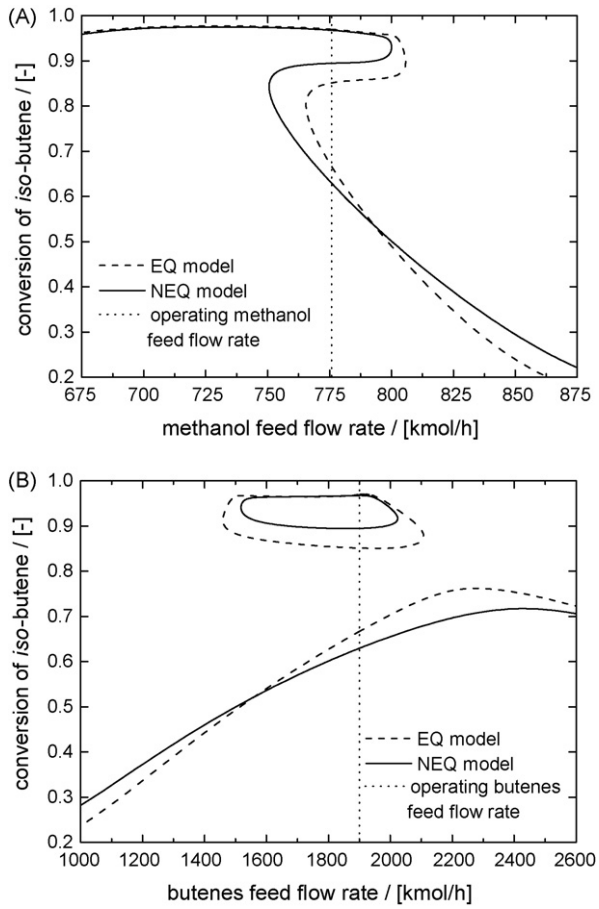

Fig. 3. Solution diagrams obtained by the EQ and NEQ models. Continuation parameter: (A) methanol feed flow rate and (B) butenes feed flow rate.

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iso-butene conversion with isolas located above these curves for both investigated models (Fig. 3B). From both solution diagrams (Fig. 3A and B) follows that the *iso*-butene conversion in the upper steady states are nearly identical for both used models. The conversion of *iso*-butene is relatively different in the lower steady state. The analysis of the methanol feed flow rate solution diagram (Fig. 3A) implies that a decrease in the methanol flow rate does not cause rapid decrease of *iso*-butene conversion. A different situation occurs when the methanol flow rate is changed to a higher value. An increase in the methanol flow rate can lead to a rapid decrease of the *iso*-butene conversion. Similar situations can be expected for the rapid decrease but also increase of the butenes feed flow.

2.4.2. Dynamic simulations

The HAZOP analysis is quite complex and time-consuming. Therefore, only one deviation, "the higher butenes feed flow rate", is analysed and discussed here. "Higher flow rate of butenes feed" means in our study: higher than 1900 kmol/h. However, what exactly does the deviation 'higher flow' mean: +5%, +10% or +15% to the designed operation value?

Fig. 4A–C shows the consequences predicted by the EQ and NEQ models for the deviation "higher butenes feed flow rate". At the time of 1 h, the butenes feed flow rate suddenly increased from the operating value of 1900–1995 kmol/h (+5%; Fig. 4A), next to the value of 2090 kmol/h (+10%; Fig. 4B) and finally to 2185 kmol/h (+15%; Fig. 4C). In all three cases, time duration of the deviation was 10 h and the reactive distillation column was forced to find a new steady state corresponding to the new value of butenes feed flow rate. At the time of 11 h, the butenes feed flow rate returned back to the operating value (1900 kmol/h). Fig. 4A shows the situation when the butenes feed flow rate was changed by about 5%. Both, EQ and NEQ, models predicted that after the butenes flow rate returns to the operating value, the reactive distillation column will return to the original steady state characterised by high conversion of *iso*-butene. Different situation is depicted in Fig. 4B, the butenes feed flow rate was changed by about 10%. After returning the butenes flow rate to the operating value, the reactive distillation column stabilised in a lower stable steady state considering the NEQ model. However, if the EQ model was used to simulate the reactive distillation column, the conversion of *iso*-butene returned to the original steady state after the perturbation. These results indicate a notable disagreement in the prediction considering the EQ and the NEQ model. Fig. 4C shows the situation when the butenes feed flow rate was changed by about 15%. Both models predicted that after the butenes flow rate returns to the operating value, the reactive distillation column will stabilise in a lower stable steady state.

From Fig. 4A–C follows that magnitude of the deviations has a significant influence on the deviation consequences; however, the consequences prediction can be different considering the EQ or the NEQ model (Fig. 4B).

In many cases, duration of the failure may dramatically affect the response of the device although this aspect is not usually investigated during a "typical" HAZOP procedure. Thus, for the next simulation, the same deviation, higher butenes feed flow rate, was taken into account. Fig. 5A and B presents dynamic simulations of an RD column, starting from the operating steady states characterised by high-conversion of *iso*-butene. At the time equal to 1 h, a 15% increase of the butenes feed flow rate was simulated (the same deviation as in Fig. 4C).

The dynamic responses for perturbations durations varying from 0.5 to 5 h were investigated using the EQ and NEQ models. The system described by the EQ model switches to the lower conversion steady state only after a perturbation longer than 3 h (Fig. 5A). However, the system described by the NEQ model switches to the lower steady state earlier, at the perturbation duration of 2 h and

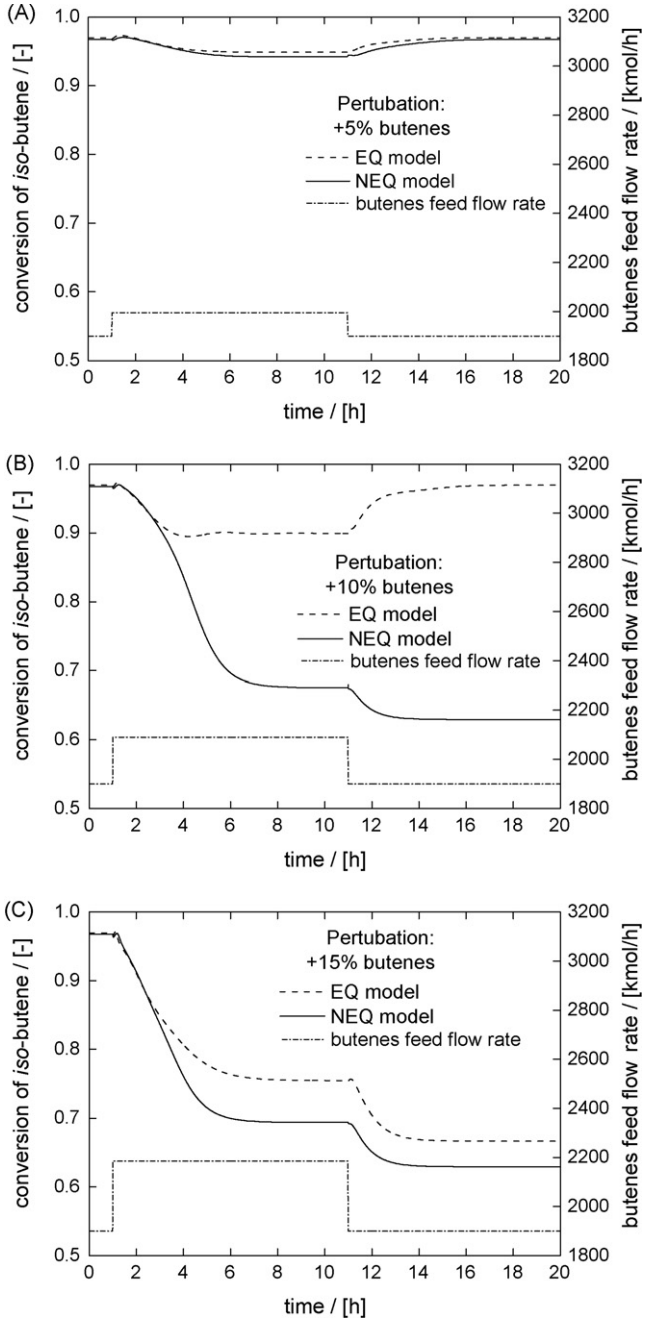

Fig. 4. Conversion changes predicted by the EQ and NEQ models caused by the step increase of the butenes feed flow rate from operating value (1900 kmol/h) and back. Deviation extension: (A) +5%, (B) +10% and (C) +15%. Deviations duration of 10 h.

more (Fig. 5B). From Fig. 5A and B, it is clear that the time durations of the feed flow rate disturbances have an extensive impact on the transitions between parallel steady states; however, the prediction of column behaviour is different assuming the EQ or the NEQ model.

The presence of multiple steady states reduces the operability and controllability of the reactive distillation column during its start-up. This is validated in Fig. 6A which represents the column start-up considering a gradual increase of the butenes feed flow rate. Before the start-up procedure, the column was filled with pure methanol. Applying this start-up procedure, after reaching the operational feed flow rate of butenes, both used models predicted column stabilisation in the steady state characterised by low conversion of *iso*-butene. To reach high

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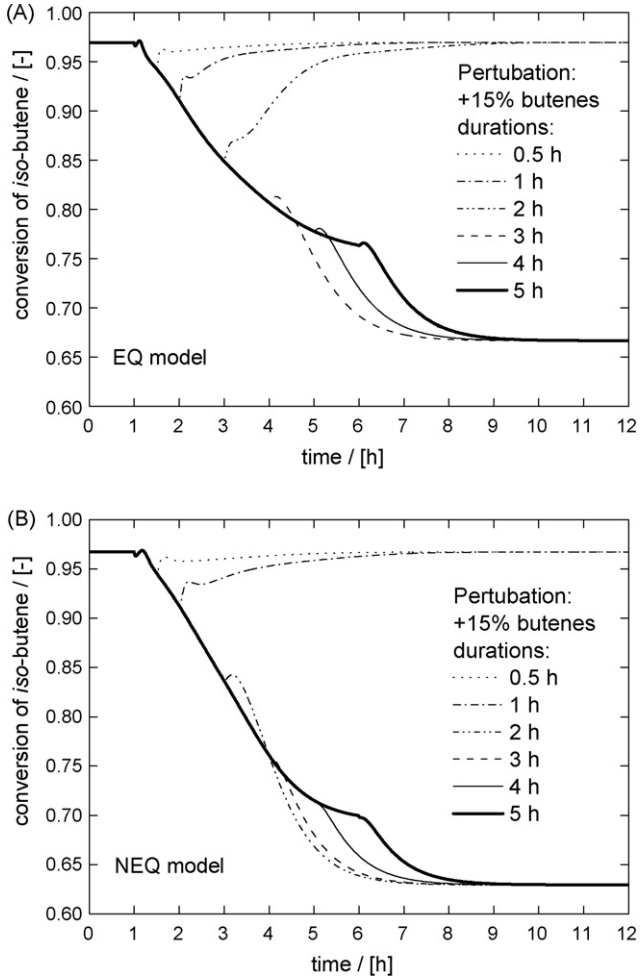

Fig. 5. Dynamic response obtained using (A) the EQ model and (B) NEQ model to an 15% increase in the butenes feed flow rate, 1 h after the simulation start. The perturbation period varied from 0.5 to 5 h.

conversion of *iso*-butene, another start-up procedure had to be applied.

With the knowledge of the solution diagram with methanol used as the continuation parameter (Fig. 3A), it was possible to lay out a new start-up strategy to switch the column to high conversion steady state. Fig. 6B presents the column start-up considering a gradual increase of the butenes feed flow rate, however, by contrast to the start-up strategy used in Fig. 6A, during the gradual increase of the butenes feed flow rate, the methanol feed flow rate into the column was fixed to the value of 720 kmol/h instead of the operating value of 775.8 kmol/h. After the operating feed flow rate of butenes was reached (1900 kmol/h), the methanol feed flow rate was changed to the operating value equal to 775.8 kmol/h (time 10 h in Fig. 6B). Simulations using both mentioned models revealed that using this start-up procedure, the column works in the higher stable steady state characterised by high conversion of *iso*-butene (Fig. 6B).

A very interesting result was obtained applying a small modification to the start-up strategy presented in Fig. 6B. During the gradual increase of the butenes feed flow rate, the methanol feed flow rate into the column was not fixed to 720 kmol/h but to 750 kmol/h. From Fig. 6C follows that the column described by the EQ model switched to the higher steady state. However, the NEQ model predicted column stabilisation in the steady

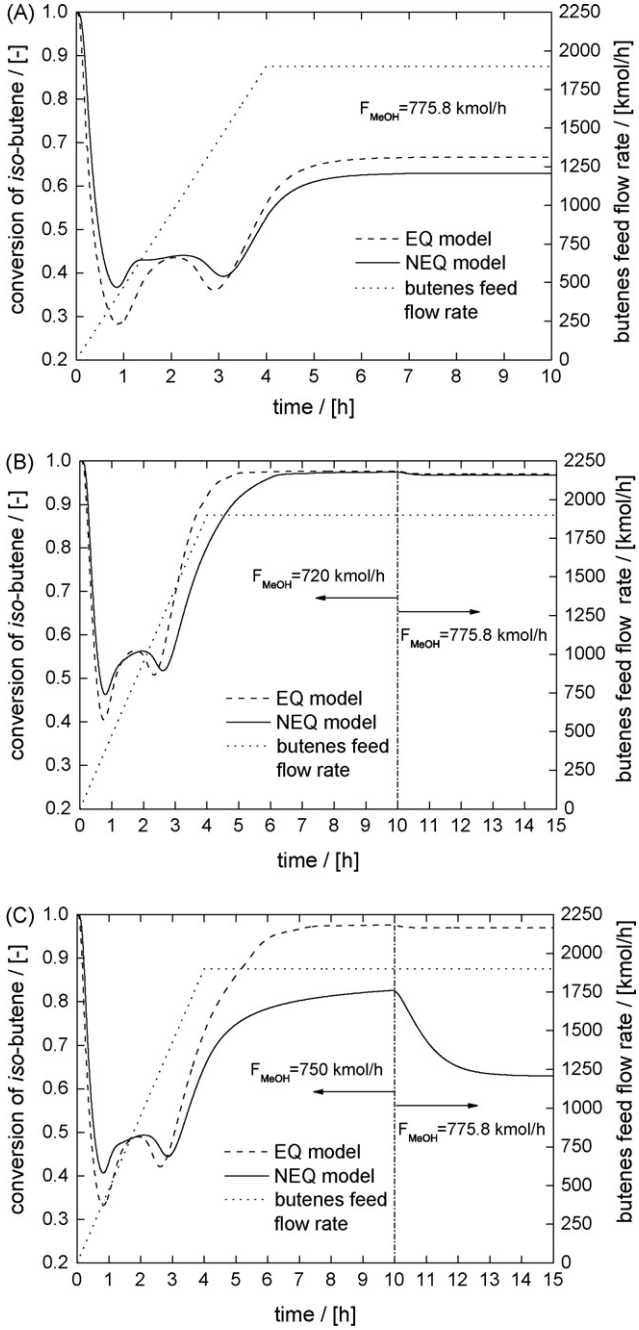

Fig. 6. The column start-up predicted by the EQ and NEQ models assuming an increase of the butenes feed flow rate to the operating value equal to 1900 kmol/h. During the gradual increase of the butenes feed flow rate is the methanol feed flow rate into the column fixed to the value: (A) 775.8 kmol/h (operating value), (B) 720 kmol/h and (C) 750 kmol/h.

state characterised by low conversion of *iso*-butene. Here is another disagreement between the EQ and the NEQ model predictions.

3. Conclusions

In this contribution, a comparison of the equilibrium and nonequilibrium models prediction during safety analysis of a reactive distillation column focusing on the identification of hazardous situations or operability problems was presented. The safety and operability analyses were based on application of the

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HAZOP procedure integrated with a mathematical model with the aim to determine the column response to deviations from normal operation conditions or during a nonstandard procedure, such as the start-up of the reactive distillation column. Duration of the failure and extension of the deviations were taken into account although this aspect is not usually investigated during a "typical" HAZOP procedure done by a HAZOP team.

For the chosen reactive distillation column configuration, multiple steady states were identified by both, the EQ and NEQ, models. At several values of butenes feed flow rate, isolated solutions branches were found. However, the proportion and localisation of the zones of multiple steady states in the solution diagrams predicted by the EQ and NEQ models could be partly different. For this reason, the EQ and NEQ models showed different responses to the HAZOP deviation "higher butenes feed flow rate" (Fig. 4B) and predicted different dynamic behaviour during the start-up procedure (Fig. 6C). The time durations of the feed flow rate disturbances had an extensive impact on the transitions between parallel steady states predicted by the EQ and NEQ models (Fig. 5A and B).

It was shown that a reliable prediction of the reactive distillation column behaviour is influenced by the complexity of the mathematical model used for its description. The EQ model is simpler, requiring a lower number of the model parameters. On the other hand, the assumption of equilibrium between the vapour and liquid streams leaving the reactor could be difficult to fulfil, especially if some perturbations of the process parameters occur. The NEQ model takes the interphase mass and heat transfer resistances into account. On the other hand, it is important to point out that prediction of the reactor behaviour is strongly dependent on the quality of the NEQ model parameters depending on the equipment design (see e.g. Švandová, Markoš, & Jelemenský, 2008).

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