

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

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Abstract

A reactive distillation column in general can exhibit multiple steady states which reduce column operability and controllability during perturbations of manipulated variables and particularly during start-up and shut down. The objective of this paper was to compare the equilibrium (EQ) and nonequilibrium (NEQ) models of a reactive distillation column, focusing on the phenomenon of multiple steady states. In particular, isolated solution branches have been found at several values of chosen reactant feed flow rate, making the column to be prone to operability and control problems. Certain perturbations in the reactants feed flow rate were found to cause transitions between parallel steady states.

Keywords: Reactive distillation; Multiple steady states; Continuation; Dynamic simulation; MTBE

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 in the case of operational failures [1].

The combination of distillative separation with a chemical reaction in a reactive distillation column leads to a complex interaction, which has been shown to cause the possible existence of multiple steady states. This phenomenon has been verified in experimental laboratory and pilot plant units [2]. In particular for methyl tertiary-butyl ether (MTBE) synthesis, various researches have focused their attention to multiple steady states [2-5]. 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 et al. [6]. In their case studies, isolated solution branches were found at several values of the Damköhler number.

2. Paper approach

2.1. Mathematical models and computational methods

For modelling reactive distillation columns, two distinctly different approaches are possible: the equilibrium (EQ) and nonequilibrium (NEQ) models [5, 7, 8]. The basic assumption of the equilibrium model is equilibrium between the streams leaving the column tray (or correlated using efficiency).

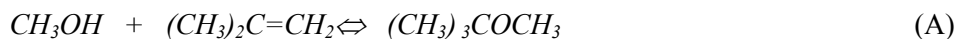
The nonequilibrium model for reactive distillation follows the philosophy of rate based models for conventional distillation [9]. The description of the interphase mass transfer is almost invariably based on the Maxwell-Stefan theory for calculation of the interphase heat and mass transfer rates [5].

Both, EQ and NEQ models consist of a set of ordinary differential and algebraic equations, which are solved by an 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 [10]
- for dynamic simulation - Fortran subroutine to solve a system of differential/algebraic equations DDASKR [11].

2.2. MTBE case study

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



where isobutene (IB) reacts with methanol (MeOH) to form MTBE in a reversible, exothermic reaction. The reaction is catalyzed by a strong ion-exchange resin. The reaction rate equation and its parameters are given by Rehfinger and Hoffmann [12]. 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 isobutene is produced. In our case study, 1-butene is used as an inert. The vapour-liquid equilibrium was calculated using the UNIQUAC model with the binary interaction parameters reported by Rehfinger and Hoffmann [12] (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 [3]. The column consists 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 is charged in the form of “envelopes” placed along the flow path length. The details of such a construction are available in paper [13]. The column pressure is 1110 kPa and the column has 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 are 775.8 kmol/h and 1976.4 kmol/h, respectively. The reflux ratio is set to 7 and the bottom flow rate to 675 kmol/h. The bottom product consists predominantly of MTBE. In the EQ model, the stage efficiency of 60% is assumed. This value corresponds closely to the calculations of the NEQ model using the *AICHE* calculation method for sieve tray mass transfer [4].

2.4. Results & discussions

The steady state behaviour of the reactive distillation column described by the EQ and NEQ models was investigated using the continuation algorithm available in paper [10]. In the solution diagrams either the methanol feed flow rate (with constant butenes feed flow rate set to the value 1976.4 kmol/h) or the butenes feed flow rate (with constant methanol feed flow rate set to the value 775.8 kmol/h) were continuation parameters. These solution diagrams are shown in Fig. 1. The bifurcation diagrams (Fig. 1A), where the methanol feed flow rate was used as a continuation parameter, indicated for both, the EQ and NEQ models, three steady states at the operating value of the methanol feed flow rate (775.8 kmol h⁻¹). These curves of *iso*-butene conversion are continuous. The bifurcation diagram (Fig. 1B.), where the butenes feed flow rate was used as a continuation parameter, indicated for both models used the same three steady states at the operating value of the butenes feed flow rate (1976.4 kmol h⁻¹) as those in Fig. 1A. However a very interesting result of this continuation are continuous curves of *iso*- butene conversion with isolas

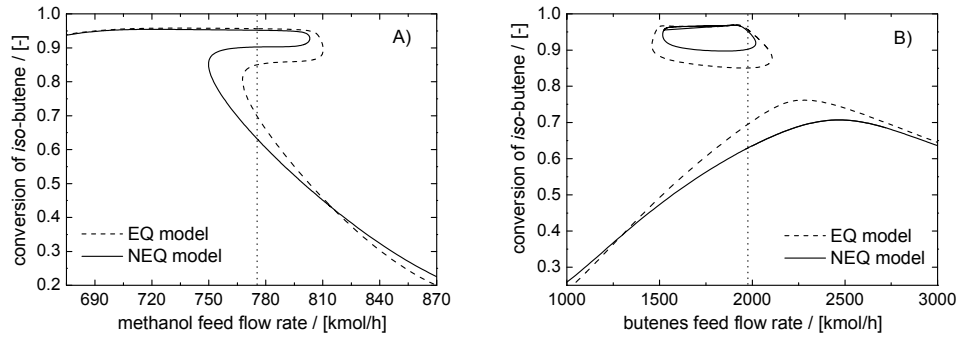


Figure 1. Comparison of solution diagrams obtained by the EQ and NEQ models. Continuation parameter: A) methanol feed flow rate, B) butenes feed flow rate.

located above these curves for both investigated models (Fig. 1B). The steady state located on these isolas can not be reached by a change of the butenes feed flow rate from steady states located on the lower continuous curve. This cognizance is validated in Fig. 2 which represents the column start-up considering a gradual increase of the butenes feed flow rate. Before the start-up procedure, the column was saturated by pure methanol. Simulations based on both models revealed that the start-up procedure switched the column to the lower stable steady states characterized by lower conversion of iso-butene (Fig. 2.). To switch the column to steady states characterized by higher conversion of iso-butene is impossible by a change of the butenes feed flow rate, but possible, for example, by a change of the methanol feed flow rate. Fig. 3 presents dynamic simulations of the RD column, starting from the steady states characterized by lower conversion of iso-butene. At the time equal to 1 h, a 5% decrease of the methanol feed flow rate was simulated. Fig. 3 shows the dynamic responses of the EQ and NEQ models for varying perturbation durations from 0.25 h to 3 h. The system described by the EQ model switches to the higher steady state, if the perturbation duration is 1 h and more.

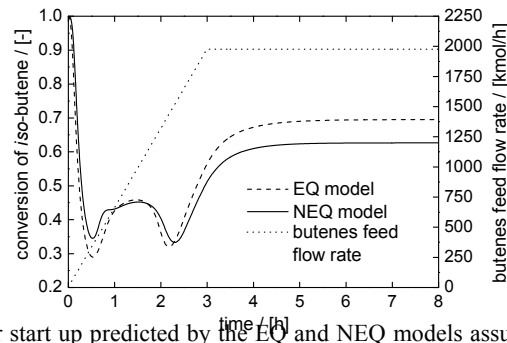


Figure 2. The reactor start up predicted by the EQ and NEQ models assuming an increase of the butenes feed flow rate to the operating value equal to 1976.4 kmol/h.

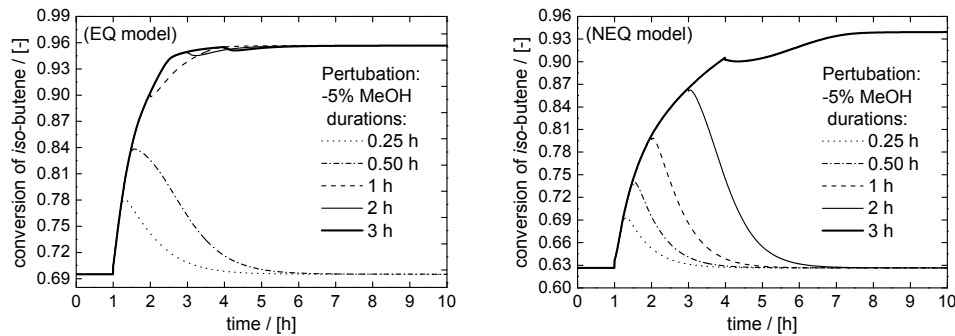


Figure 3. Dynamic response obtained using the EQ (on the left hand side) and NEQ (on the right hand side) models to a 5% decrease in the methanol feed flow rate, 1 h after simulation start-up. The perturbation period is varied from 0.25 to 3 h.

However, the system described by the NEQ model reverts back to the initial steady state for all perturbation durations shorter than 3 h. It is clear, that the EQ and NEQ models predicted different start-up strategies to higher steady states. Because of isola existence at several values of butenes feed flow rate, the perturbations of butenes feed flow rate can result in an irreversible loss of *iso*-butene conversion. Fig. 4. presents dynamic simulations of the RD column, starting from the operating steady states characterized by high-conversion of *iso*-butene. At the time equal to 1 h, an 8% increase of the butenes feed flow rate was simulated. The dynamic responses for varying perturbations durations from 0.5 to 5 h are different using the EQ and NEQ models. The system described by the EQ model switches to the lower-conversion steady state only after perturbation, which is longer than 4 h. However, the system described by the NEQ model switches to the lower steady state earlier, if the perturbation duration is 1 h and more.

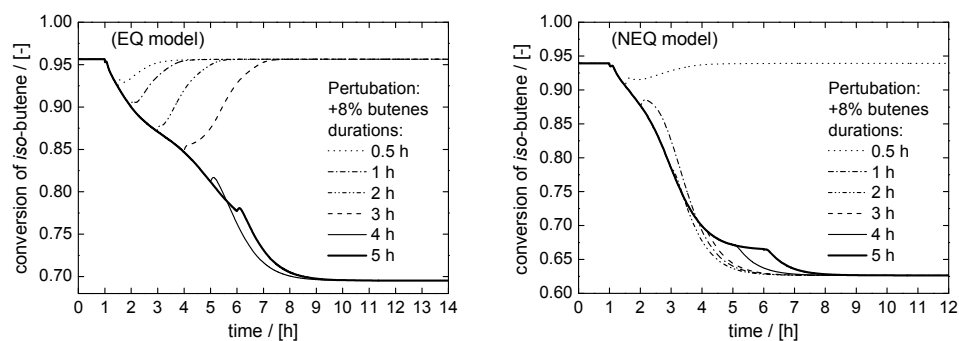


Figure 4. Dynamic response obtained using the EQ (on the left hand side) and NEQ (on the right hand side) models to an 8% increase in the butenes feed flow rate, 1 h after simulation start-up. The perturbation period is varied from 0.5 to 5 h.

3. Conclusions

For the chosen reactive distillation column configuration, multiple steady states were identified by both the EQ and NEQ models. In particular, at several values of butenes feed flow rate, isolated solutions branches are found. However, localization 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 show qualitatively different responses to feed flow rates disturbances of methanol and butenes and predicted different start-up strategy to higher steady states. The time durations of feed flow rate disturbances have an extensive impact on transitions between parallel steady states predicted with the EQ and NEQ models. 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 into account the interphase mass and heat transfer resistances. On the other hand, it is important to point out that prediction of the reactor behaviour is strongly dependent on the quality of NEQ model parameters, depending on the equipment design.

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