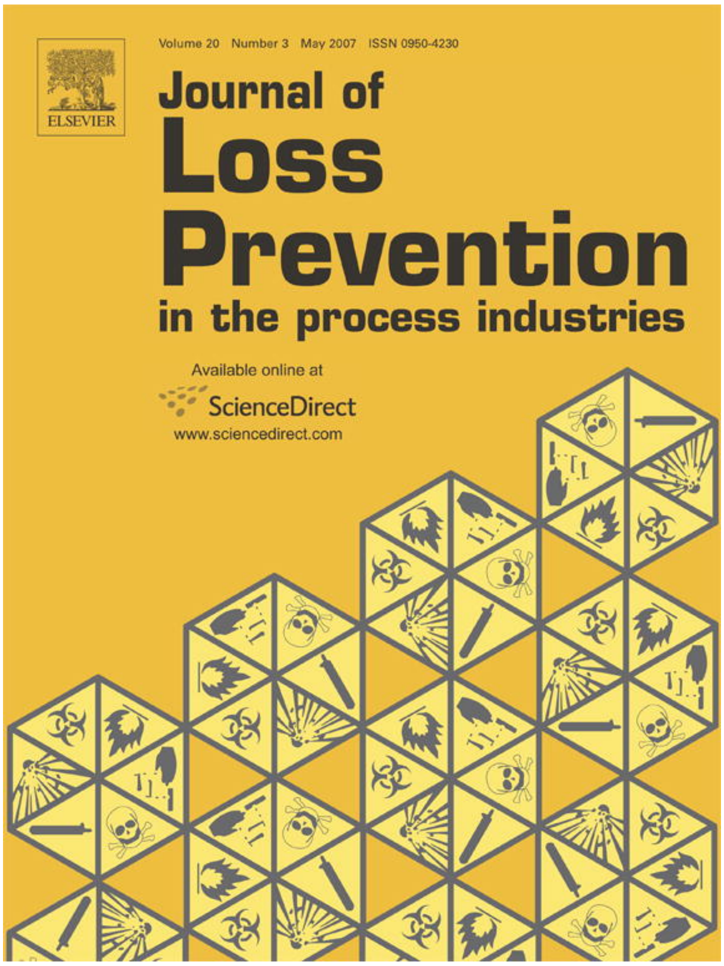
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Model-based HAZOP study of a real MTBE plant

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Abstract

Integration of a mathematical model approach with hazard and operability (HAZOP) analysis is presented in this contribution. The presented analysis is based on the mathematical modelling of a process unit, where both the steady-state analysis (including continuation and bifurcation analyses), and the dynamic simulation are used. The main benefit of this integration is the ability to perform a detail safety analysis for a relatively complicated process. Such an approach may dramatically decrease the possibility that several sources of hazard will be overlooked. Of course, the presented methodology may also seriously reduce the time necessary for the hazard identification process. In this paper, a methyl *tertiary*-butyl ether (MTBE) production unit was chosen to identify potential hazard and operational problems of a real process. This simplified case-study unit consists of two investigated types of equipment: a tubular fixed bed reactor and a reactive distillation column.

Keywords: Safety analysis; Model-based HAZOP approach; Fixed bed reactor; Reactive distillation column; MTBE

1. Introduction

Hazard and operability (HAZOP) is one of the best and most rigorous techniques for identification of hazard and operability problems in a chemical plant. The HAZOP procedure formally examines step by step all equipment as well as deviations from their normal operation conditions and considers what failures can appear. The HAZOP report includes all the deviations, their causes, consequences in equipment performance, analysis of such consequences, implemented protection (active and/or passive), and resulting suggestions. It can be successfully applied not only for existing plants, but also for new designed technologies and equipment. On the other hand, two essential drawbacks of the HAZOP study exist. The prime drawback of the HAZOP study is related to the possibility, that hazards and operability problems may be overlooked. HAZOP requires many hours of work of a team of experienced engineers, and it is not easy to record the engineering reasoning, basic input information, or the results. Therefore, the application of the HAZOP technique to a detailed chemical plant design is a complex and time consuming task. Both of these drawbacks can be reduced by integration of a model approach into HAZOP. In the last 20 years, a lot of research effort has been dedicated to the development of computer-based analysis methods which can be roughly divided into two main groups: expert and model-based approaches.

A typical expert approach for the HAZOP study, which usually comprises three or four knowledge bases and an interface engine, was proposed in the work of Shimada, Suzuki, and Sayama (1996). Other expert approaches with additional facilities have been developed by Weatherill and Cameron (1989) and Goring and Schecker (1993).

In contrast to the knowledge-based approach, the model-based approach has gained more importance in the last years. It is based on the description of a chemical plant using a mathematical model. This procedure holds promise of greatly reducing the time and effort required in HAZOP making the study more smooth and detailed and minimising the influence of human factors. The model-based approach with a set of mathematical equations derived from the quantitative description of a chemical

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plant seems to be the most straightforward procedure. Usually, the HAZOP analysis does not consider duration and amplitude of the deviations generated during the reactor 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 10 min or more, or is it only an impulse? Is this decrease continuous at some rate? Answers to these questions may be obtained by using an appropriate mathematical model. In such a model, the extent of deviations may be easily incorporated and possible consequences investigated.

In the presented paper, the model-based approach, including the HAZOP methodology, was applied on an methyl *tertiary*-butyl ether (MTBE) production plant. This case study is linked with a real industrial process and consists of two main operation units: a tubular reactor and a reactive distillation column. In the first step, a mathematical model of both types of equipment was formulated. Next step was to perform a safety analysis using steady-state and dynamic approaches (Molnár, Markoš, & Jelemenský, 2005). By the steady-state approach, the stability of the system and the locus of operating conditions were analysed. By the dynamic approach, the time and way of shifting from one steady state to another steady state due to failure deviation was analysed. By these approaches the parameter sensitivity of the system to the failures of operating parameters was also investigated. Finally, the results of safety analysis were reproduced and utilised in HAZOP studies. The contribution of this work is to demonstrate that combination of a standard identification method, like HAZOP, together with mathematical modelling has the potential to become a very practical and robust tool for the reactor safety analysis.

However, it is important to point out, that investigation of multiple steady states for the chosen system is impacted by the selection of an adequate mathematical model and is strongly dependent on the parameters which describe physical properties, kinetic, interphase resistance of mass and heat transfers, etc.

2. Case study

The presented safety analysis methodology is demonstrated on the case study of a simplified methyl *tertiary*-butyl ether (MTBE) production plant case study. MTBE is produced according to the following reaction scheme:

$$CH_3OH + (CH_3)_2C = CH_2 \Leftrightarrow (CH_3)_3COCH_3,$$

where isobutene (IB) reacts with methanol (MeOH) to form MTBE in a reversible exothermic reaction. The reaction is catalysed by strong cationic ion-exchange resin. The reaction rate is given by Rehfinger and Hoffmann (1990). Possible side-reactions have been ignored. The reaction is usually carried out in the presence of inert components from the upstream processing where IB is produced. In our case study, 1-butene (1-B) is used as an inert. For the calculation of mixed physicochemical properties, an internal software library was employed. 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-B and the other components). Physicochemical properties of all pure components were taken from the HYSYS 2.1 database.

2.1. Plant description

The MTBE plant depicted in Fig. 1 consists of two major items: a tubular fixed bed reactor and a reactive distillation column.

The fixed bed reactor is filled with catalyst and the design operation parameters are set in the following way:

- the fresh methanol molar flow rate into the fixed bed reactor (stream 1) at the value of 95 kmol/h,
- the mixture of IB (18.7%) and 1-B (81.3%) molar flow rate into the fixed bed reactor (stream 2) at the of value of 460 kmol/h,
- the mixture of streams 1 and 2 is preheated in the heat exchanger at the temperature of 306 K,
- the fixed bed reactor reflux (stream 4) at the value of 0.5,
- the fixed bed reactor pressure at the value of 1940 kPa.

The reactive distillation column (RDC) configuration chosen for the simulations consists of a total condenser, 15 sieve trays (1 rectifying stage, 8 reactive stages and 6 stripping stages), and a partial reboiler. On each of the reactive stages, 50 kg of the catalyst is charged and the design operation parameters are set as follows:

- the fresh methanol molar flow rate into the RDC (stream 3) at the value of 20 kmol/h,
- stream 3 is preheated in the heat exchanger to the temperature of 306 K,
- the reflux ratio of reactive distillation at the value of 3,
- the bottom flow rate from RDC (stream 5) at the value of 90 kmol/h,
- the column pressure at the value of 1110 kPa.

3. Mathematical models and computational methods

Owing to mild temperature profiles and negligible differences (both, temperature and concentration) between fluid bulk and solid catalyst, a pseudo-homogeneous model was chosen for the description of the reactor behaviour. This model describes only the axial profile of radially averaged temperatures and concentrations. Since the only transport mechanism taken into account is convection, the model is referred to as a plug-flow model.

To describe the steady state and dynamic behaviour of a reactive distillation column, an equilibrium mathematical

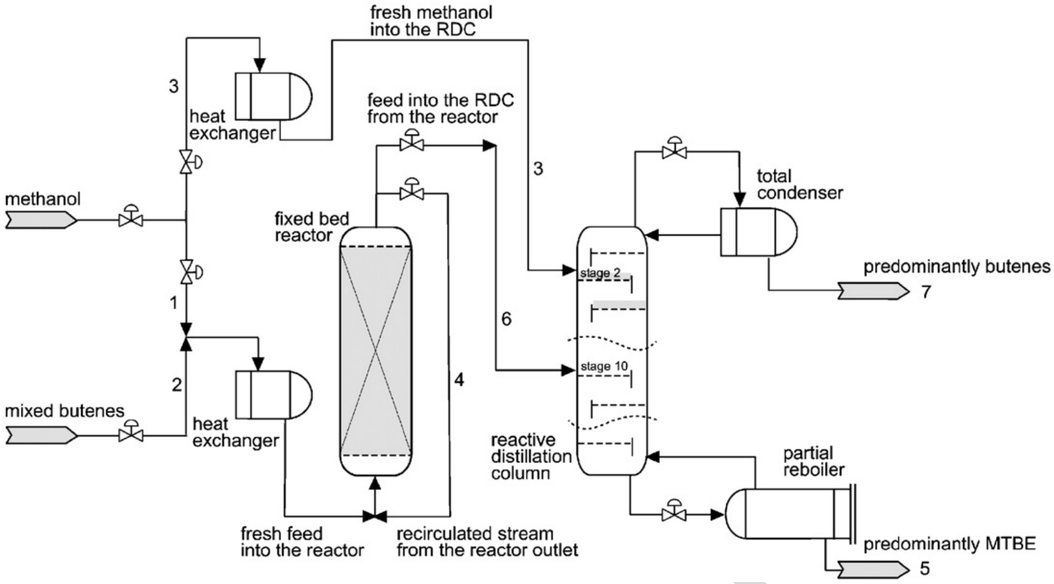

Fig. 1. Schematic flow diagram of the MTBE plant.

model was chosen (see Taylor & Krishna, 1993). The basic assumption of this model is the equilibrium between the streams leaving the column tray. Equations involved in the equilibrium model are the component material balances, equations of phase equilibrium, summation equations, and heat balance of the reactor (MESH equations).

The mathematical model for description of the fixed bed reactor behaviour consists of a set of partial differential equations (PDE), and the model for description of the reactive distillation column consists of a set of ordinary differential and algebraic equations (DAE) which are solved by developed DYNHAZ software based on C++ code and a FORTRAN code, using:

- the method of finite differences—for discretisation of the set of PDE,
- backward differential formulas up to the 5th order with a step controller—for the time integration (of PDE and DAE) implicit schemes,
- LAPACK library—for the solving system of sparse linear equations,
- modification of CONT—continuation and stability analysis (see Kubíček, 1976) for the identification of multiple steady states.

4. Results and discussions

Possible deviations during the HAZOP study are generated by rigorous questioning, prompted by a series of standard "guidewords" applied to the intended design (see Kletz, 1999). After the guideword is matched with a parameter, a deviation is generated. The next step in the 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 the large interval of operating parameters are obtained by a continuation algorithm. This algorithm is able to identify the quality of a steady-state solution (stability analysis) and the multiple steady states (Kubíček, 1976). The information about trajectories and conditions which can shift the system from one steady state to another can be obtained by dynamic analysis.

For the proposed safety analysis methodology of the presented MTBE plant (Fig. 1), it is necessary to investigate all deviations of all operating parameters; temperature, composition and flow rate of all feed streams in to the system and recirculated streams, as well as all deviations of their combinations and their consequences, but this is out of the range of this paper. Therefore, only two parameters; the inlet molar flow rate of fresh methanol into the fixed bed reactor (stream 1) and the inlet molar flow rate of fresh methanol into the reactive distillation column (stream 3) are analysed and discussed here.

The monitored output parameters are: IB conversion in the fixed bed reactor, IB conversion in the reactive distillation column and total IB conversion.

The fixed bed reactor conversion of IB is defined in our case study as: the difference between the 'fresh IB molar feed flow rate into the fixed bed reactor (stream 2)' and the 'IB molar feed flow rate into the reactive distillation column (molar flow rate of IB in stream 6)' divided by the 'fresh IB molar feed flow rate into the fixed bed reactor (stream 2)'.

The reactive distillation column conversion of IB is defined in our case study as: the difference between the 'IB molar feed flow rate into the reactive distillation column (molar flow rate of IB in stream 6)' and the 'molar flow rate of IB in the output streams from the reactive distillation column (molar flow rates of IB in streams 5 and 7)' divided by the 'IB molar feed flow rate into the reactive distillation column (molar flow rate of IB in stream 6)'.

The total conversion of IB is defined in our case study as: the difference between the 'fresh IB molar feed flow rate into the fixed bed reactor (stream 2)' and the 'molar flow rate of IB in the output streams from the reactive distillation column (molar flow rate of IB in streams 5 and 7)' divided by the 'fresh IB molar feed flow rate into the fixed bed reactor (stream 2)'.

4.1. Parameter no. 1: 'fresh methanol feed flow rate into the fixed bed reactor (stream 1)'

Designed operation value: 95 kmol/h

4.1.1. Steady-state analysis

The steady states solution diagrams of the fixed bed reactor conversion of IB, reactive distillation column conversion of IB and the total conversion of IB as a function of fresh methanol flow rate into the fixed bed reactor (stream 1) is depicted in Fig. 2a–c. The solution diagram of the reactor conversion of IB as a function of fresh methanol feed flow rate into the reactor (Fig. 2a) has a typical 'S' profile and the maximum number of steady states for some values of methanol feed flow rate is three. The solution diagrams of the RDC conversions and of the total conversion (Fig. 2b and c) are more complicated and the maximum number of steady states for some values of methanol feed flow rate is five. From these results, it follows that the fresh methanol feed flow rate into the fixed bed reactor has a significant influence on the conversion of

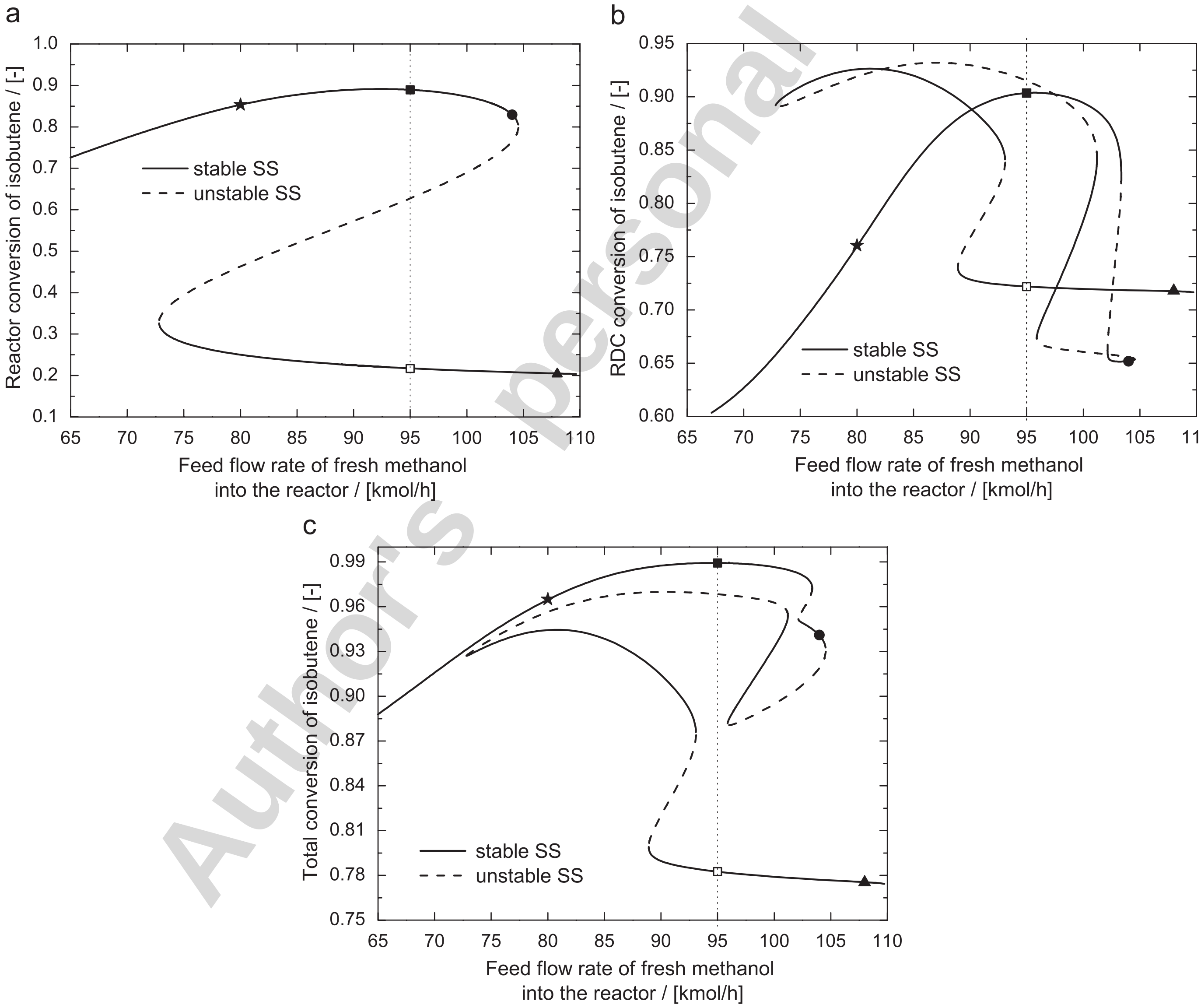

Fig. 2. The solution diagrams of (a) fixed bed reactor conversion, (b) reactive distillation column conversion and (c) total conversion, of IB as a function of fresh methanol feed flow rate into the fixed bed reactor. Dotted line—designed operation value of methanol feed flow rate into the reactor, solid square—desired operating point, empty square—lower operating point, solid circle—steady state for methanol flow rate equal to 104 kmol/h, solid triangle—steady state for methanol flow rate equal to 108 kmol/h, solid star—steady state for methanol flow rate equal to 80 kmol/h.

IB in the fixed bed reactor and also on the conversion of IB in the reactive distillation column. From Fig. 2a–c follows that for the designed operating feed flow rate of 95 kmol/h (dotted line in Fig. 2a–c), three steady states (two stable, one unstable) are identified. The desired operating point is the point with the greatest conversion of IB (solid square in Fig. 2a–c). Fig. 2a indicates that with an increase of the feed flow rate of methanol from the desired operating point, the conversion of IB in the reactor follows an upper stable steady-state branch up to the value depicted by the circle. If a further increase of the feed flow rate of fresh methanol occurs, a new steady state is reached on the lower stable steady-state branch depicted by the triangle in Fig. 2a. On the other hand, the conversion of IB in the RDC (Fig. 2b) is more complicated. Which of the stable steady-state branches will be reached in the RDC by this further increase of the feed flow rate of fresh methanol depends on the conversion in the fixed bed reactor. If the conversion in the fixed bed reactor is close to the stable steady state marked by the solid circle in Fig. 2a then the conversion in the RDC column is on the stable steady-state branch marked by the solid circle in Fig. 2b. If the conversion in the fixed bed reactor is on the lower stable steady-state branch (marked by the solid triangle in Fig. 2a) then the conversion in the RDC column is on the stable steady-state branch marked by the solid triangle in Fig. 2b.

A similar situation occurs for the total conversion (Fig. 2c). Without dynamic analysis, it is hardly predictable at which stable steady-state branch the system will be stabilised. The steady states solution diagrams indicate that the system under consideration has a strong nonlinear character and during dynamic analysis, it would be highly sensitive to the extent of any operating parameter deviation.

4.1.2. Dynamic analysis

Deviation: 'higher flow rate of fresh methanol into the fixed bed reactor'

'Higher flow rate of fresh methanol into the fixed bed reactor' means in our study: higher than 95 kmol/h (intended), but maximal 110 kmol/h (the transport capacity). However, what exactly does the deviation 'higher flow' mean: +5% or +15% to the designed operation value?

9.5% higher flow rate of fresh methanol into the fixed bed reactor

When a step change of the methanol flow into the fixed bed reactor from 95 (intended) to 104 kmol/h was considered (i.e. by 9.5% higher than the designed operation value) a new stable steady state was achieved (Fig. 3). This achieved steady state corresponds with the steady state depicted in the solution diagrams (Fig. 2a–c) by a solid circle. The solution diagram of the fixed bed reactor conversion of IB (Fig. 2a) indicates that at this moment, the reactor works in the steady state which is localised on

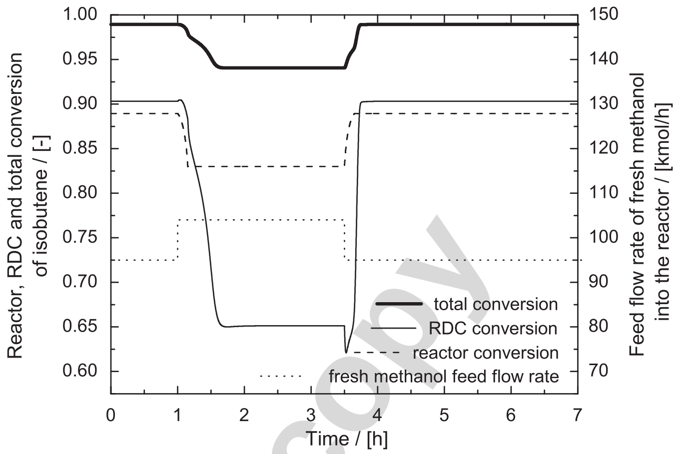

Fig. 3. Deviation: 9.5% higher flow rate of fresh methanol into the fixed bed reactor and back.

the upper stable steady-state branch (solid circle in Fig. 2a). However, the solution diagrams of the reactive distillation column conversion (Fig. 2b) show that for the methanol feed rate equal to 104 kmol/h, the reactive distillation column works in the steady state which is characterised by the lowest possible conversion of IB (solid circle in Fig. 2b). At this moment, the total conversion of IB is equal to 94% (Fig. 3) and corresponds with the steady state which is depicted by the solid circle in Fig. 2c. The consequence of this deviation is a loss of the MTBE production. After returning the methanol feed flow rate into the reactor to the designed operation value (time 3.5 h in Fig. 3), the system works again in the higher original steady state, without additional loss of the MTBE production.

13.7% higher flow rate of fresh methanol into the fixed bed reactor

When the methanol feed flow rate into the reactor was changed from 95 to 108 kmol/h (i.e. by 13.7% higher than the designed operation value), a new stable steady state was achieved (Fig. 4). This new steady state corresponds with the steady state which is depicted in the solution diagrams (Fig. 2a–c) by a solid triangle. For methanol feed flow rate equal to 108 kmol/h only one steady state is possible. This steady state is characterised by low conversion of IB in both types of equipment. An interesting result of this simulation is that after returning the methanol feed flow rate into the reactor to the operating value (time 3.5 h in Fig. 4), the system was stabilised at a different stable steady state as before the deviation (lower steady state, empty square in Fig. 2a–c). Even though the methanol feed flow rate reaches the operation flow rate again, the system works in a lower steady state and a loss of the MTBE production occurs.

Deviation: 'lower flow rate of fresh methanol into the fixed bed reactor'

When a step change of the methanol flow into the fixed bed reactor from 95 (intended) to 80 kmol/h was

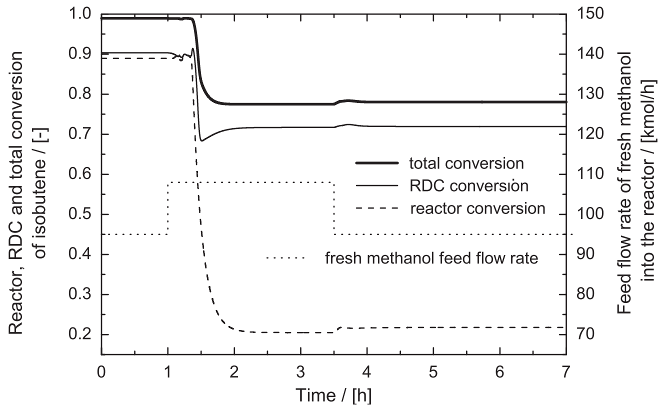

Fig. 4. Deviation: 13.7% higher flow rate of fresh methanol into the fixed bed reactor and back.

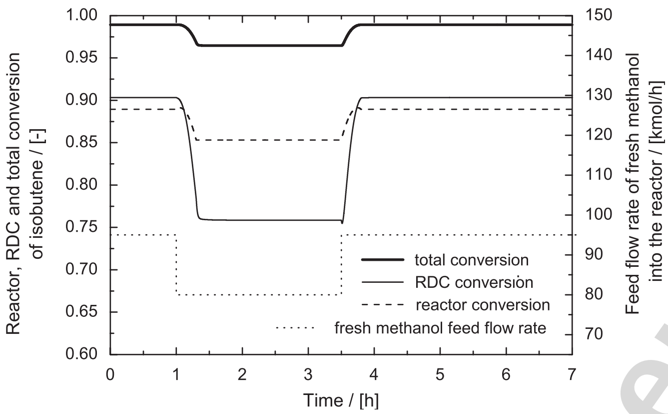

Fig. 5. Deviation: 15.8% lower flow rate of fresh methanol into the fixed bed reactor and back.

considered (i.e. by 15.8% lower than the designed operation value), a new stable steady state was achieved (Fig. 5). This newly achieved steady state corresponds with the steady state depicted in the solution diagrams (Fig. 2a–c) by a solid star.

The solution diagram of the fixed bed reactor conversion of IB (Fig. 2a) indicates that at this moment, the reactor works in the steady state which is localised on the upper stable steady-state branch (solid star in Fig. 2a). However, the solution diagrams of reactive distillation column conversion (Fig. 2b) show that for methanol feed rate equal to 80 kmol/h, the reactive distillation column works in the steady state characterised by the lowest possible conversion of IB (solid star in Fig. 2b). At this moment, the total conversion of IB is equal to 96% (Fig. 3) and corresponds with the steady state which is depicted by a solid star in Fig. 2c. The consequence of this deviation is a loss of the MTBE production. After returning the methanol feed flow rate into the reactor to the operating value (time 3.5 h in Fig. 5), the system works again in the higher original steady state, without any additional loss of the MTBE production.

4.2. *Parameter no. 2: 'fresh methanol feed flow rate into the reactive distillation column'*

Designed operation value: 20 kmol/h

4.2.1. *Steady-state analysis*

All input parameters of the fixed bed reactor influence not only the reactor behaviour, but also the reactive distillation column, because a part of the reactor outlet is also the feed stream into the reactive distillation column. However, input parameters of the reactive distillation column influence only the reactive distillation column and do not affect the operation of the fixed bed reactor. One of these parameters is: 'fresh methanol feed flow rate into the reactive distillation column'. For chosen design operation

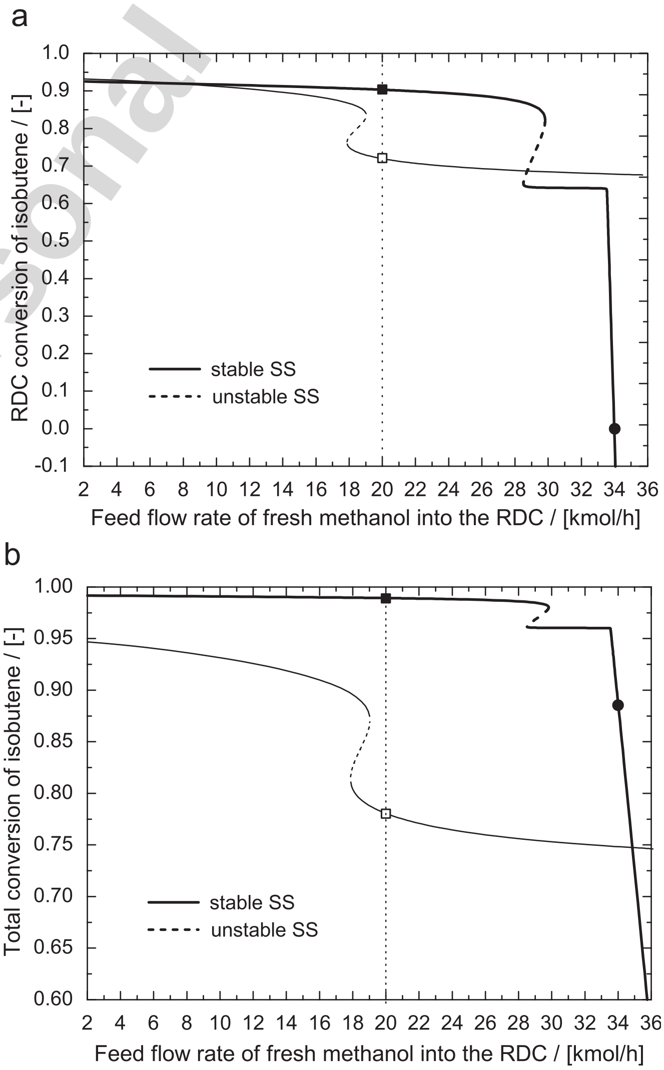

Fig. 6. The solution diagrams of (a) reactive distillation column conversion and (b) total conversion, of IB as a function of fresh methanol feed flow rate into the reactive distillation column (thick curve corresponds with the situation when the fixed bed reactor works at the upper-stable operating point (solid square in Fig. 2a) and the thin curve corresponds with the situation when the fixed bed reactor works at the lower stable operating point (empty square in Fig. 2a)).

conditions, the fixed bed reactor can operate in two stable steady states (solid and empty squares in Fig. 2a). Consequently, the steady-state solution diagrams of the reactive distillation column conversion of IB and the total conversion of IB as a function of fresh methanol flow rate into the reactive distillation column (see Fig. 6a and b) contain two independent curves. The thick curve corresponds with the situation when the fixed bed reactor works at the upper-stable operating point (solid square in Fig. 2a) and the thin curve corresponds with the situation when the fixed bed reactor works at the lower stable operating point (empty square in Fig. 2a). Both curves in Fig. 6a and b indicate the presence of multiple steady states. Solution diagrams (Fig. 6a and b) show that if the fixed bed reactor is working in the upper-operating steady state, the methanol flow rate into the reactive distillation column may not be higher than approximately 30 kmol/h, because of a very fast decrease of IB conversion in the reactive distillation column.

4.2.2. Dynamic analysis

Deviation: 'higher flow rate of fresh methanol into the reactive distillation column'

Higher flow rate of fresh methanol into the reactive distillation column means in our study: higher than the designed operation value. When a step change of the methanol flow into the reactive distillation column from the designed value (20 kmol/h) to 34 kmol/h was considered (i.e. by 70% higher than the designed operation value), a new stable steady state was achieved (Fig. 7). This steady state corresponds with the steady state which is depicted in the solution diagrams (Fig. 6a and b) by a solid circle. At this moment, the conversion of IB in the reactive distillation column is equal to zero and the total conversion of IB is equal to the conversion in the fixed bed reactor. An additional increase of the methanol feed flow rate into the reactive distillation column (>34 kmol/h) caused a backward reaction and decomposition of MTBE in the reactive distillation column. The consequence of this deviation is the total loss of the MTBE production in the RDC. After returning the methanol feed flow rate into the RDC to the designed operation value (time 20 h in Fig. 7), the system works again in the higher original steady state, without any additional loss of the MTBE production in the RDC.

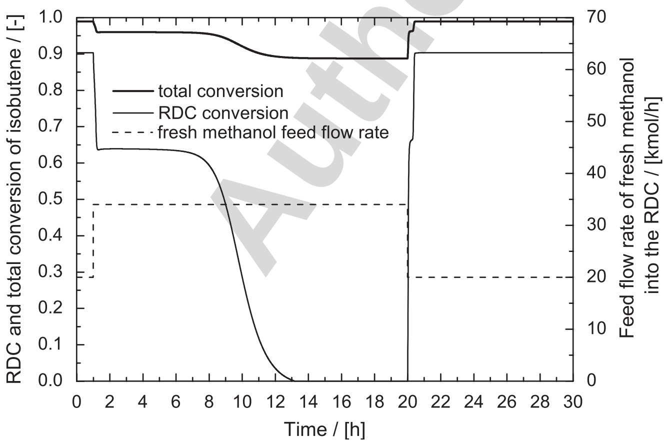

Fig. 7. Deviation: 70% higher flow rate of fresh methanol into the reactive distillation column.

5. Conclusions

In this paper, a new methodology of safety and operability analysis was presented. The basis of this methodology is the fusion of mathematical modelling with a standard hazard identification method (HAZOP). The integration of mathematical modelling into the HAZOP study may potentially lead to the identification of some unexpected deviations and may radically decrease the time necessary for the hazard identification process.

A MTBE production unit was chosen for the demonstration of this methodology. Due to the complexity and extensity of the HAZOP analysis, only two parameters, the 'inlet molar flow rate of fresh methanol into the fixed bed reactor' and the 'inlet molar flow rate of fresh methanol into the reactive distillation column' were analysed. The steady state analysis has shown that the solution diagrams for both investigated parameters indicated multiple steady states. The dynamic analysis has revealed that a different extent of a deviation has a radical influence on the system behaviour not only during the deviation, but also after the correction of the deviation to the designed operation value. All derived HAZOP deviations along with their consequences may be analysed in a similar way by the approach presented.

The advantage of such an approach is that it provides the complex overview of the set of the steady states solutions together with the dynamical response to the failure deviations. This overview can help to understand and explain some unpredictable behaviour of a system. The authors of this paper are also members of an HAZOP team and so are aware of the problem that this behaviour could be registered by the system operators but could not be specified in a classical HAZOP study as the system is not supposed to have more possible stable steady states.

The results of this procedure present a wide multidimensional view of the chemical plant safety. This information could directly serve to the examination of the industrial equipment safety, or may be used as a robust basis for a subsequent ordinary HAZOP study.

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