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Design, optimization and safety analysis of a heterogeneous tubular reactor by using the HAZOP methodology

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Abstract

In this contribution, a model approach to Hazard and Operability (HAZOP) analysis is presented. This analysis is based on the mathematical modelling of a process unit, where both the steady-state analysis, (including the analysis of the steady states multiplicity and stability) and the dynamic simulation are used. A heterogeneous tubular reactor for the production of ethylene oxide and a reactor for the production of MTBE were chosen to identify potential hazards for a real system. The computer code DYNHAZ consisting of a process simulator and a generator of the HAZOP algorithm was developed.

Keywords: tubular reactor, dynamic simulation, steady states analysis, HAZOP

1. Introduction

Hazard and Operability (HAZOP) analysis is a well know method for performing hazard analysis of a chemical plant [1]. It is a difficult, labour and knowledge intensive activity that can benefit from automation approach. In the last 20 years a lot of research effort has been dedicated to the development of computer-based analysis methods roughly distinguishing 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 by Shimada et al. [2]. In contrast to the knowledge-based approach, the model-based approach has gained more importance in the last years. It describes the chemical plant behaviour using a mathematical model and only focuses on the model examination. This procedure holds promise of greatly reducing the time and effort required in HAZOP, making the study more smooth and detailed, and minimizing the influence of human factors. As the first, Parmar and Lees [3] attempted to automate the HAZOP study by using qualitative propagation equations for initiation and termination events.

2. Paper approach

The presented studies were aimed to develop a model based approach including the HAZOP methodology based on a very complex mathematical model of a tubular heterogeneous reactor. In the hazard identification process, both the steady-state analysis and the dynamic simulation were provided. Combination of the standard identification method, like HAZOP, together with the mathematical modelling, has the potential to become a very practical and robust tool for the reactor safety analysis. To simulate a real industrial system, the reactor for ethylene oxide production and the reactor for MTBE synthesis have been chosen. For this purpose the computer code DYNHAZ was developed comprising a process simulator and a generator of the HAZOP algorithm.

2.1. Case studies

2.1.1. Partial Oxidation of Ethylene to Ethylene Oxide case study

The first selected system is a partial oxidation of ethylene to ethylene oxide in a fixed bed catalytic reactor. The reaction takes place in an excess of ethylene. Two main by-products CO_2 and H_2O are formed according to the following reaction scheme:

$$O_2 + 2C_2H_4 \rightarrow 2C_2H_4O \qquad \text{(A)}$$

$$O_2 + 1/3C_2H_4 \rightarrow 2/3CO_2 + 2/3H_2O \qquad \text{(B)}$$

The kinetic data have been adopted from the work [4], the operating conditions, reactor geometry and the transport parameters are shown in paper [5]. The reaction rates are of first order with respect to oxygen and zero-th order with respect to ethylene. Both reactions are exothermic. Activation energy and reaction enthalpy of the latter reaction are higher as for the former reaction. It means, that an increase of temperature will accelerate the rate of reaction (B) with an increase of temperature in the reaction and decrease of the selectivity to the desired product. A one-dimensional heterogeneous model with axial dispersion was used. External heat and mass transfer between the fluid and the solid phase was assumed. However, internal diffusion and heat transfer inside the catalyst particle were neglected.

2.1.2. MTBE case study

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

$$CH_3OH \quad + \quad (CH_3)_2C{=}CH_2 \Leftrightarrow \; (CH_3)_3COCH_3 \qquad \text{(C)}$$

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 [6]. 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. Physico- chemical properties of all pure components were taken from the HYSYS 2.1 database.

2.2. Results & discussions

2.2.1. Partial Oxidation of Ethylene to Ethylene Oxide case study

In this simplified example, the algorithm used only one HAZOP keyword - oxygen inlet concentration, for which the following HAZOP deviations are possible to generate: No oxygen flow (-100%), Lower oxygen flow (<-50% -1%>), Higher oxygen flow (<1% 100%>). With the utilization of the heuristic interpretation of the dynamic results it is possible to generate the consequences of three deviations summarized in Table 1. The computer code performed a set of dynamic simulations with a different amplitude of this deviation to analyze the possible consequences of such oxygen concentration changes.

Deviation	Consequence
No inlet oxygen flow -	Not dangerous, but a technological problem, conversion is too low (in this case the value of conversion is zero)
Lower inlet oxygen flow -	Not dangerous, but a technological problem, conversion is too low
Higher inlet oxygen flow -	may be dangerous if the deviation is higher than 20% - possible run-away

Table 1. Possible generated consequences of the deviation “inlet oxygen flow”

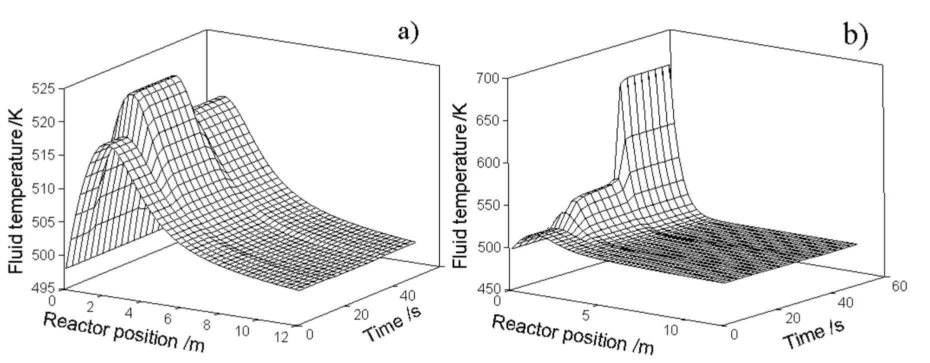

Figure 1.Dynamic evolution of the temperature profile along the reactor for different positive deviations from the input oxygen molar flow rate: a) 20 %, b) 23

Because it is not possible to show all of the results, only the deviation “higher oxygen concentration” is presented here. For illustration, in Fig. 1. is shown the temperature profile development after increasing the inlet concentration by about +20% (Fig. 1a) and +23% (Fig. 1b) up to the normal operation concentration. The simulation data show, that the consequence of a slight increase of the deviation above 20 % would cause a run-away of the reactor temperature due to the ethylene oxide auto-ignition at temperatures exceeding 700 K. Furthermore, DYNHAZ is able to calculate the locus of the process variables, at which the run-away effect could occur. In Fig. 2 the dashed line represents the locus of the run-away for the chosen pair of process variables.

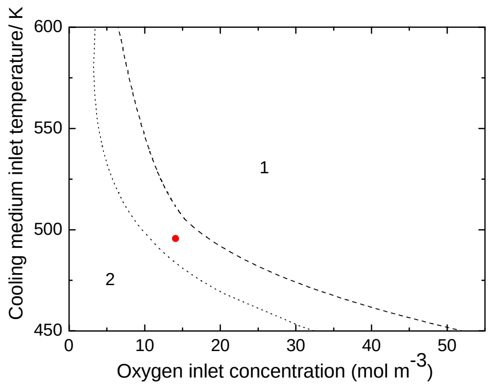

Figure 2. Locus of the run-away effect for the plot cooling medium temperature vs. oxygen inlet concentration circle corresponds to the normal reactor operation point, dashed line limits the region of the possible reactor run-away

2.2.2. MTBE case study

DYNHAZ is able to investigate the steady state behaviour of a tubular reactor using the continuation algorithm [7,8]. Therefore it allows to identify the regions where multiple steady states may occurr. For illustration, two bifurcation diagrams are presented. The former bifurcation diagram (Fig. 3.b), 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 (98 kmol h^{-1}). The latter (Fig.3.b) shows the bifurcation diagram for the reactor inlet temperature. The presence of multiple steady states phenomenon reduces equipment operability and controllability, particularly during perturbations of the investigated parameters. For example, the analysis of the bifurcation diagram of the parameter - methanol feed flow rate implies, that after increasing the methanol feed flow rate over 105 kmol h^{-1}, the reactor shifts to a lower steady state and the MTBE conversion decreases dramatically. This situation is shown in Fig. 4.a. A different situation occurs, if the methanol feed flow rate increases to the value of 103 kmol h^{-1}. In this case the limit point (104.53kmol.h^{-1}) will not be reached thus, the reactor will be at the higher steady state (Fig. 4.b). Therefore, after the methanol feed flow rate returns back to the operating value (98 kmol h^{-1}), the reactor will be stabilized at the original steady state (compare Figs 3. a and 3.b).

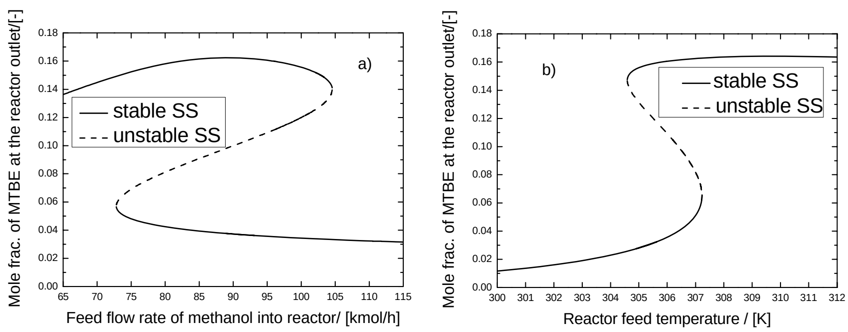

Figure 3. Solutions diagrams for the continuation parameter a) Feed flow rate of methanol into the reactor b) Reactor feed temperature

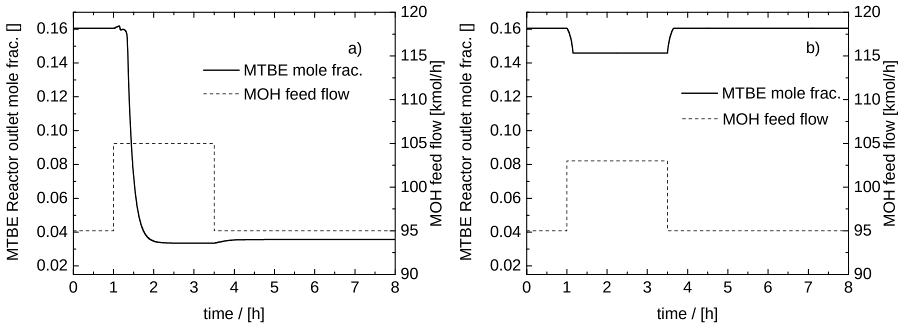

Figure 4.Comparison of evolution diagrams of a failure of MOH flow rate for 2.5 hours duration. a) step change to 105 kmol.h^{-1} b) step change to 103 kmol.h^{-1}

3. Conclusions and future work

In the present paper, we tried to show a new methodology for the hazard identification. The basis of this methodology is the integration of software tools, primarily designed for the safety analysis of chemical reactors, into the HAZOP study. This integration is useful for identification of consequences for some deviations, and for the suggestion of corrective actions. Furthermore, it can directly serve for the examination of the reactor safety, or can be used as a robust basis for the subsequent, ordinary HAZOP study.

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