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Combining HAZOP with dynamic simulation—Applications for safety education

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Abstract

A quantitative variation of the hazard and operability analysis (HAZOP) procedure is demonstrated. The process is divided into sections and dynamic models of the separate sections are prepared. Those models are used in the framework of the HAZOP procedure to determine the magnitude of the deviations from normal operation conditions that may lead to serious accidents and to test design modification to improve the safety characteristic of the process. A process involving an exothermic reaction conducted in a semi-batch reactor is used to demonstrate the advantages of the proposed procedure and its application for safety education and operator training. The programs used for simulating the reactor are available at: ftp://ftp.bgu.ac.il/shacham/OctanoneProd/.

It is shown that the use of those programs can enhance considerably the safety education by providing tools for systematic screening of process deviation associated with possible hazardous events, determining the threshold values that may lead to such events and enabling the examination of a particular design for the adequate safe range of operation.
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1. Introduction

Learning to predict and prevent chemical process hazards is an essential part of the chemical engineer's education. Mannan et al. (1999) discuss in detail the various aspects of process safety education. They point out that safety in the process industry is of primary importance and is critical to the industry's continuing license to operate. The number of accidents happening in the process industry is unacceptable and recently there have been many requests to develop standards for reducing the frequency and severity of chemical accidents. The university plays obviously a critical role in achieving this objective.

Mannan et al. (1999) suggest that students should take specific courses on process safety engineering. However, process safety should also be incorporated into existing chemical engineering courses, such as design, reaction kinetics and thermodynamics. The objective in putting such a great emphasis in safety issues is shifting the paradigm to safety being the engineer's second nature. It is very important to make it clear to the students that safety considerations are essential components of process and equipment design and operations.

Hazard and operability analysis (HAZOP) is a widely used procedure for process hazards analysis (Dash & Venkatasubramanian, 2003; Kletz, 1999; Lawley, 1974). HAZOP is carried out by a multidisciplinary team of experts in a qualitative manner. The new process is examined systematically, section by section, looking for inadequacies in design, which may lead to serious accidents. A series of guide words (such as "None", "More of", "Less of", etc.) are used to ensure that all the potential deviations from normal operating conditions are considered. For each deviation the possible causes are listed and the consequences and actions required are considered. Often the action required is a change of the design in order to reduce the probability of a particular deviation, or to

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reduce the severity of its consequences. In a few cases, where deviation from normal conditions may lead to catastrophic events, HAZOP is often followed by a detailed hazard analysis (HAZAN, Kletz, 1999), where the probability for the occurrence of such events is evaluated.

Incorporating HAZOP into process safety education is a real challenge as often the demonstration of the potential consequences of deviations from normal operating conditions is rather difficult. Combining HAZOP with dynamic simulation can provide the means for investigating those consequences. Dynamic simulation also enables the student to suggest and try various strategies dealing with the emergency situation and allows rapid investigation of the effectiveness of these strategies in preventing culmination of components' failure into serious accidents.

The use of dynamic simulation in safety analysis of chemical processes has been recently documented, for example, by Chiappetta, Clarizia, and Drioli (2006), Graf and Schmidt-Traub, (1999), Lou, Chandrasekaran, and Smith (2006), Ruiz, Canton, Nougues, Espuna, and Puigjaner (2001) and Nemeth, Cameron, and Hangos (2005). The use of steady-state analysis and dynamic simulation as a complement in the HAZOP study of chemical reactors has been suggested recently by Svandova, Jelemensky, Markos, and Molnar (2005).

We have developed a "Quantitative HAZOP" approach which is more adequate for educational applications than the qualitative HAZOP procedure. Using this approach, dynamic simulation is integrated into the HAZOP framework. First a model, which represents the process under normal operating conditions, is developed. This model is extended and modified during the HAZOP procedure, so that it can represent the process behavior adequately when deviations from normal conditions are introduced. The process deviations are defined in quantitative terms and the limit where the deviation leads to severe consequences is determined.

The proposed procedure is demonstrated in the next section, using a semi-batch reactor in which 2-octanone is produced from 2-octanol (van Woezik & Westerterp, 2000, 2001). In this reactor, small deviations from the appropriate operating conditions may cause sudden reaction of accumulated product 2-octanone, followed by reaction rate and temperature runaway. A dynamic model of the reactor was solved using the Polymath 6.1[1] numerical software package.

2. Oxidation of 2-octanol in a semi-batch reactor—preparation and validation of the simulation model

The nitric acid oxidation of 2-octanol to 2-octanone followed by further oxidation of 2-octanone to carboxylic acids was studied by van Woezik and Westerterp (2000, 2001). The oxidation of 2-octanol is carried out in a two-phase reaction system: an organic liquid phase, which initially contains 2-octanol, in contact with an aqueous nitric acid phase in which the reactions takes place. The reaction can be described with the following equations:

$$A + B \xrightarrow{r_1} P + 2B, \tag{1}$$

$$P + B \xrightarrow{r_2} X, \tag{2}$$

where A is 2-octanol, P is 2-octanone, X are the further oxidation products and B is the nitrosonium ion, which also causes an autocatalytic behavior. The reaction is carried out in a semi-batch reactor in which aqueous nitric acid is initially present, and the organic component 2-octanol (A) is added at a constant feed rate until a desired molar ratio of the reactants is reached. The 2-octanol reacts to form 2-octanone and carboxylic acid. The heat of reaction is removed by a coolant, which flows through an external jacket.

Under normal operating conditions, when the temperature in the reactor does not exceed the limit of approximately 0 °C throughout the reaction, only a very small fraction (about 7.5%) of the 2-octanone is converted to carboxylic acids. However, if the temperature at any time exceeds approximately 5 °C, runaway conditions develop, which may lead to a maximal temperature of over 200 °C, and conversion of essentially all of the 2-octanone to carboxylic acid.

The mathematical model of the reactor and its cooling jacket is shown in Table 1. This model is based on the model presented by van Woezik and Westerterp (2001).

A change to the original model is the use of dimensional variables in the balance equations instead of dimensionless ones used by van Woezik and Westerterp (2001). We preferred to use dimensional variables, as it has been shown by Eizenberg Shacham, and Brauner (2004) that the use of such variables in HAZOP studies is preferable as it provides more meaningful results. A detailed model of the cooling jacket has also been added to the reactor model.

The reactor model is fairly complex. In order not to repeat the detailed explanation of the model (which is provided by van Woezik & Westerterp, 2001) we have added the equation numbers as they appear in the original reference into Table 1 (these numbers are shown inside parentheses).

The model in Table 1 is presented in a format which enables copying and pasting the column of the equations directly into the differential equation solver program of the Polymath 6.1 package. Running this model will provide the solution for the reactor under normal operating conditions. The model equations are of the form: (output variable) = g (input variables, constants), where g is a function. Table 1 provides also a clear documentation of the mathematical model as the "Comment" column includes definition of the output variable of the equation, including its units.

The model equations are presented in an order consistent with the principles of model building (Shacham, Brauner,

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