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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.

Keywords: HAZOP; HAZAN; Dynamic simulation; Temperature runaway

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,

[1]Polymath is copyrighted by M. Shacham, M. B. Cutlip and M. Elly (http://www.polymath-software.com/).

Table 1
Mathematical model of 2-octanol oxidation example

No.[a]	Equation	Comment (output variable definition)
1	$t(0) = 0.0001$	Starting time
2	$t(f) = 72\,000$	Final time (s)
3	$d(N_p)/d(t) = (r_1 - r_2) \times V_{r0}/(1 - \text{Epsd})$	Number of moles of 2-octanone (P) from mole balance
4	$N_p(0) = 0$	Number of moles of 2-octanone (P) at $t = t_0$
5	$d(N_x)/d(t) = r_2 \times V_{r0}/(1 - \text{Epsd})$	Number of moles of carboxylic acids (X) from mole balance
6	$N_x(0) = 0$	Number of moles of carboxylic acids (X) at $t = t_0$
7 (3)	$r_1 = k_1 \times \text{CaOrg} \times \text{CbAq} \times (1 - \text{Epsd})$	Reaction rate of A and B to P (kmol/m^3/s)
8 (4)	$r_2 = k_2 \times \text{CpOrg} \times \text{CbAq} \times (1 - \text{Epsd})$	Reaction rate of P and B to X (kmol/m^3/s)
9	$V_{r0} = 1.5$	Initial volume in a reactor (m^3)
10	$\text{Epsd} = V_{dos1}/(V_{dos1} + V_{r0})$	Volume fraction of dispersed phase
11 (5)	$k_1 = \text{maA1} \times \exp(-\text{E1perR}/T_r - \text{m}_1 \times H)$	Specific reaction rate 1
12 (5)	$k_2 = \text{mpA2} \times \exp(-\text{E2perR}/T_r - m_2 \times H)$	Specific reaction rate 2
13 (6)	$\text{CaOrg} = (\text{Theta} \times \text{NaF} - N_p - N_x)/(V_{dos1} \times \text{Theta})$	Concentration of (A) in org. phase (kmol/m^3)
14 (8)	$\text{CpOrg} = N_p/(V_{dos1} \times \text{Theta})$	Concentration of (P) in org. phase (kmol/m^3)
15 (7)	$\text{CbAq} = (N_p + Y \times \text{NaF})/V_{r0}$	Concentration of (B) in aq. phase (kmol/m^3)
16	$V_{dos1} = 0.6$	Final volume of the dose (m^3)
17	$\text{maA1} = 10^5$	Pre-exponential factor reaction 1 (m^3/kmol/s)
18	$\text{mpA2} = 10^{10}$	Pre-exponential factor reaction 2 (m^3/kmol/s)
19	$\text{E1perR} = 11\,300$	Activation temperature reaction 1 (K)
20	$\text{E2perR} = 12\,000$	Activation temperature reaction 2 (K)
21	$m_1 = 6.6$	Hammett's reaction rate coefficient reaction 1
22	$m_2 = 2.2$	Hammett's reaction rate coefficient reaction 2
23	$H = -0.6221 - 3.7214 \times \text{wt} - 1.5714 \times \text{wt}^2$	Hammett's acidity function
24	$\text{Theta} = \text{if } (t \leqslant t_{dos}) \text{ then } (t/t_{dos}) \text{ else } (1)$	Dimensionless time up to $t = t_{dos}$
25	$\text{NaF} = V_{dos1} \times \text{RhoOctan}/\text{MwOctan}$	Total amount of 2-octanol (A) fed (kmol)
26	$Y = 0.035$	Initial concentration of nitrosonium ion $Y = \text{Nb0}/\text{NaF}$
27	$\text{wt} = \text{Nn} \times \text{Mw}/(V_{r0} \times \text{RhoAcid})$	Mass concentration of nitric acid sol. (%/100%)
28	$t_{dos} = 36\,000$	Dosing time (s), 10 h
29	$\text{RhoOctan} = 820.7$	Density of 2-octanol (kg/m^3)
30	$\text{MwOctan} = 130.23$	Molar mass of 2-octanol (kg/kmol)
31	$\text{Nn} = \text{CnAq} \times V_{r0}$	Number of moles of HNO_3 (kmol)
32	$\text{Mw} = 63$	Molar mass of HNO_3 (kg/kmol)
33	$\text{RhoAcid} = 1500$	Density of pure nitric acid (kg/m^3)
34	$\text{CnAq} = (\text{NnO} - Y \times \text{NaF} - N_p - 2 \times N_x)/V_{r0}$	Concentration of HNO_3 in the aq. Phase(kmol/m^3)
35	$\text{NnO} = V_{r0} \times \text{Percent} \times \text{RhoAcid}/\text{Mw}$	Initial number of mole of HNO_3 (kmol)
36	$\text{Percent} = 0.6$	Initial mass concentration of nitric acid sol. (%)
37	$D(T_r)/d(t) = (Q_r + Q_{dos} + Q_{cool})/\text{Gamma}$	Temperature in the reactor (K) from energy balance
38	$T_r(0) = 260$	Temperature in the reactor at $t = t_0$ (K)
39	$Q_r = Q_{nol} + Q_{none}$	Sum of the heat of reaction the reactions (W)
40 (15)	$Q_{dos} = \text{Phi} \times \text{RhoCP}_{dos} \times (T_{dos} - T_r)$	Heat input due to reactant addition (W)
41 (16)	$Q_{cool} = \text{UA}_{cool} \times (T_{cool} - T_r)$	Heat removed by the cooling jacket (W)
42	$\text{Gamma} = \text{Gamma0} + \text{RhoCP}_{dos} \times \text{Phi} \times t$	Total heat capacity of the system (J/K)
43 (21)	$Q_{nol} = r_1 \times V_{r0} \times H_{nol}/(1 - \text{Epsd})$	Heat of reaction 1 (W)
44 (22)	$Q_{none} = r_2 \times V_{r0} \times H_{none}/(1 - \text{Epsd})$	Heat of reaction 2 (W)
45	$\text{Phi} = V_{dos1}/t_{dos}$	Volumetric flow rate of the feed (m^3/s)
46	$\text{RhoCP}_{dos} = 2 \times 10^6$	Heat capacity of dose (J/m^3/K)
47	$T_{dos} = 293.15$	Temperature of feed dose (K)
48	$\text{UA}_{cool} = \text{UA0} + (\text{UA1} - \text{UA0}) \times \text{Theta}$	Cooling surface heat transfer coefficient (W/K)
49	$\text{Gamma0} = 5.4 \times 10^6$	Initial heat capacity of the system (J/K)
50	$H_{nol} = 160 \times 10^6$	Specific heat of reaction 1 (J/kmol)
51	$H_{none} = 520 \times 10^6$	Specific heat of reaction 2 (J/kmol)
52	$\text{UA0} = 1500$	Initial cool. surface heat transfer coefficient (W/K)
53	$\text{UA1} = 2100$	Final cool. surface heat transfer coefficient (W/K)
54	$D(T_{cool})/d(t) = (F_w \times (T_{cool\_IN} - T_{cool}) - Q_{cool}/(\text{RhoCoolant} \times \text{CpCoolant}))/Vj$	Cooling water outlet temperature (K) from jacket energy balance
55	$T_{cool}(0) = 273.15$	Coolant exit temperature at $t = t_0$ (K)
56	$F_w = 100/60 \times 10^{-3}$	Flow rate of coolant (m^3/s)
57	$T_{cool\_IN} = 260$	Initial coolant temperature (K)
58	$\text{RhoCoolant} = 1000$	The density of coolant (kg/m^3)
59	$\text{CpCoolant} = 4183$	Heat capacity of coolant (J/kg/K)
60	$Vj = 1.5$	Volume of the jacket (m^3)

[a]Equation numbers in parentheses refer to the numbers in van Woezik and Westerterp (2001).

& Cutlip, 2000). The equations are aggregated around the balance equations. A balance equation is added to the model first. Next, the input variables of this equation are specified. Some variables are expressed as constitutive equations (e.g. reaction rates, heat and mass transfer rates), others as thermodynamic property correlations or constants. The addition of new equations is continued as long as there are still input variables that have not been defined as output variables. This structure of the mathematical model makes the model easy to understand and easy to modify for conducting HAZOP studies.

In Table 1, the initial and final values of the independent variable (t, time) are defined first. Next the mole balance equations that yield the amount of desired product, 2-octanone (in line 3) and the undesired carboxylic acid (in line 5), are entered. The definition of the initial value for the output variable follows the equation definition.

The equations, that specify input variables associated with the mass balance relationships, are listed in lines 7–36 of Table 1. The next balance equation, the energy balance on the reactor content, which defines the temperature in the reactor as output variable, is entered in line 37 with initial value specified in line 38. The input variables associated with the reactor's energy balance equation are specified in lines 39–53. The balance equation on the cooling jacket, which yields the outlet temperature of the cooling media, and the associated input variable specifications are shown in lines 54–60 of Table 1.

Simulating the operation of the semi-batch reactor using the numerical values shown in Table 1 (which represent normal operating conditions) yields the results shown in Table 2 for the key variables. In this table the initial, minimal, maximal and final values of the variables are shown. It can be seen that under such operational conditions the temperature of the cooling media never exceeds 0 °C and the temperature in the reactor only slightly exceeds this value ($T_{r,max} = 1.31$ °C). Both temperatures are reduced toward the end of the reaction. The plot of the temperature variation in the reactor is shown in Fig. 1.

The final amount of the desired product, 1-octanol, is $n_P = 3.16$ kmol (as shown in Table 1) and the final amount of the carboxylic acids is $n_X = 0.26$ kmol. The variation of the amounts of the desired and the undesired products is shown in Fig. 2.

The values obtained at normal operational conditions are consistent with the results of van Woezik and Westerterp (2001). Thus, the correctness of the model has been verified and it is possible to proceed with the preparation of the simulation program.

3. Oxidation of 2-octanol in a semi-batch reactor—preparation of the user interface for the simulation program

To carry out the "quantitative HAZOP" studies, a large number of runs of the simulation program has to be carried out. In order to carry out those runs more efficiently, a graphical user interface (GUI) has to be added to the simulation program. To this aim the program has been exported to MATLAB[2] where special tools are available for creating a GUI.

One of the options provided by the Polymath program is the conversion of the mathematical model into a MATLAB function. Polymath also provides a "template" for running this function in order to verify the correctness of the model in the MATLAB function format. Part of the program, which is used for testing the MATLAB representation of the mathematical model, is shown in Table 3. This program obtains the solution for the case of normal operating conditions and displays numerical and graphical results for the variables N_p, N_x, T_r and T_{cool}.

After the correctness of the MATLAB results has been verified the MATLAB program has to be modified to enable the change of parameters, as required by the HAZOP procedure, and the presentation of the results via a GUI.

The GUI that was developed for the semi-batch reactor simulation program is shown in Fig. 3. The interface allows the change of the following parameter values: coolant inlet temperature, initial temperature in the reactor and jacket (at the start of the batch), temperature of the 2-octanol feed (dose temperature), flow rate of the coolant, time duration of 2-octanol feed (dosing time) and duration of the batch. There is also an option to completely stop the coolant flow for a pre-specified period of time. Additional parameters can be changed, if needed, by changing the MATLAB program.

The tabular results presented include initial, minimal, maximal and final values of the moles of the reactant, the desired and the undesired products and the reactor temperature. The same variables and the temperature in the cooling jacket are also presented in a graphical form.

Using this GUI the effect of the parameter changes in the reactor's behavior can be investigated. Let us consider, for example, the change of the coolant's inlet temperature to 265 K (−8.15 °C). The results obtained for this case are summarized in Table 4 and Figs. 4 and 5. It can be seen that after about 4 h and 26 min (16 000 s) temperature runaway occurs and the temperature in the reactor rises up to 410.16 K (137 °C). The sudden rise of temperature causes the entire accumulated product of 2-octanone to be converted to carboxylic acids. After that the reaction rate diminishes considerably causing fast cooling of the reactor, which enables production of a small amount of 2-octanone in the later stages of the reaction.

4. Oxidation of 2-octanol in a semi-batch reactor—quantitative HAZOP

After preparing the simulation program, a quantitative HAZOP analysis can be carried out by dividing the process

[2]MATLAB is a trademark of The Math Works, Inc. (http://www.mathworks.com).

Table 2
Semi-batch reactor operation in normal operating conditions

	Variable	Initial value	Minimal value	Maximal value	Final value
1	t (time, s)	0.0001	0.0001	72000	72000
2	N_p (2-octanone, mol)	0	0	3.122345	3.122345
3	N_x (carboxylic acids, mol)	0	0	0.2520688	0.2520688
4	T_r (reactor temperature, K)	260	260	274.571	261.6412
5	T_{cool} (cooling temperature, K)	273.15	260.3828	273.15	260.3828

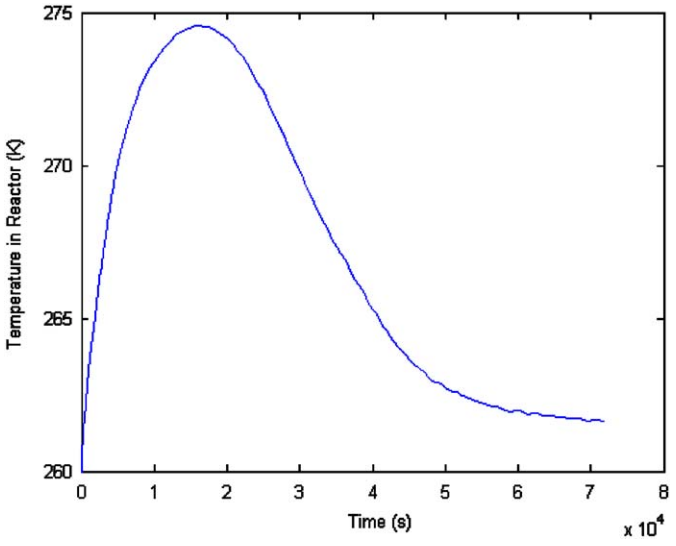

Fig. 1. Temperature variation in the reactor in normal operating conditions.

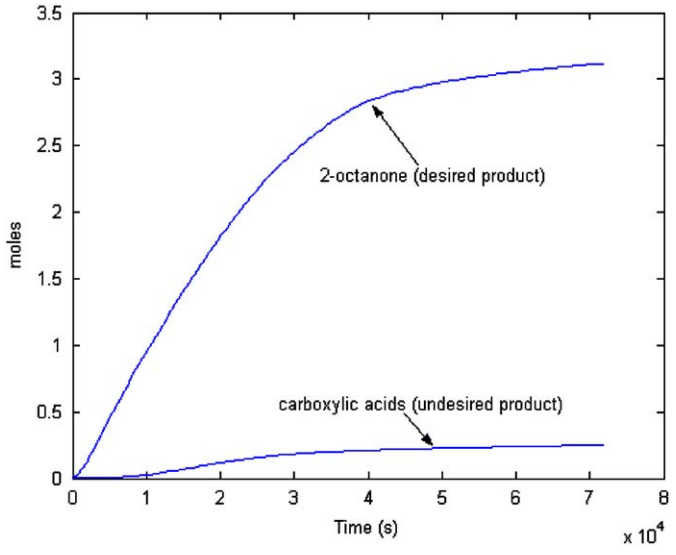

Fig. 2. Molar amounts of the desired and the undesired products in normal operating conditions.

into various sections and using the guide words: None, More of, Less of, etc. to generate a list of potential equipment failures. Selecting, for example, the cooling jacket section, the following list of potential failures should

Table 3
Part of the MATLAB program for checking the mathematical model

No.	Command/comment
1	function SemiBatchDispl
2	clear, clc, format short g, format compact
3	$t_{span} = [0.0001 \times 7.2E+04]$; % range for the independent variable
4	$y0 = [0; 0; 260; 273.15]$; % initial values for the dependent variables
5	disp('Variable values at the initial point');
6	disp(['t = ' num2str(tspan(1))]);
7	disp('y dy/dt');
8	disp([$y0$ ODEfun($t$span(1),$y0$)]);
9	[t,y] = ode45(@ODEfun,tspan,$y0$);
10	for i = 1:size(y,2)
11	disp(['Solution for dependent variable y' int2str(i)]);
12	disp(['t y' int2str(i)]);
13	disp([t y(:,i)]);
14	plot(t,y(:,i));
15	title(['Plot of dependent variable y' int2str(i)]);
16	$x$label('Independent variable (t)');
17	$y$label([' Dependent variable y' int2str(i)]);
18	pause
19	end
20	%- - - - - - - - - - - - - - -
21	function dYfuncvecdt = ODEfun(t, Yfuncvec);
22	N_p = Yfuncvec(1);
23	N_x = Yfuncvec(2);
24	T_r = Yfuncvec(3);
25	T_{cool} = Yfuncvec(4);

be considered: (1) no flow in the cooling jacket (None); (2) reduction of the flow rate into the cooling jacket (Less of); (3) reduction of the effective heat transfer rate (Less of); (4) reduction of the effective jacket volume (Less of) and (5) increase of the inlet temperature of the cooling media (More of).

Let us take for example the reduction of the flow rate into the cooling jacket. To investigate the effect of this failure, various coolant flow rates can be specified in the GUI (shown in Fig. 3). The results can be summarized in a table, as shown in Table 5. It can be seen that the coolant flow rate can be reduced to about 1/6th of its normal value without causing temperature runaway and loss of significant amount of 2-octanone. Only when the flow rate is reduced to 70 l/min temperature runaway occurs.

In Table 6 results of a similar study concerning the reduction of the effective heat transfer rate are shown. This rate can decrease with time because of scale accumulation in the heat transfer surface. It can be seen that when

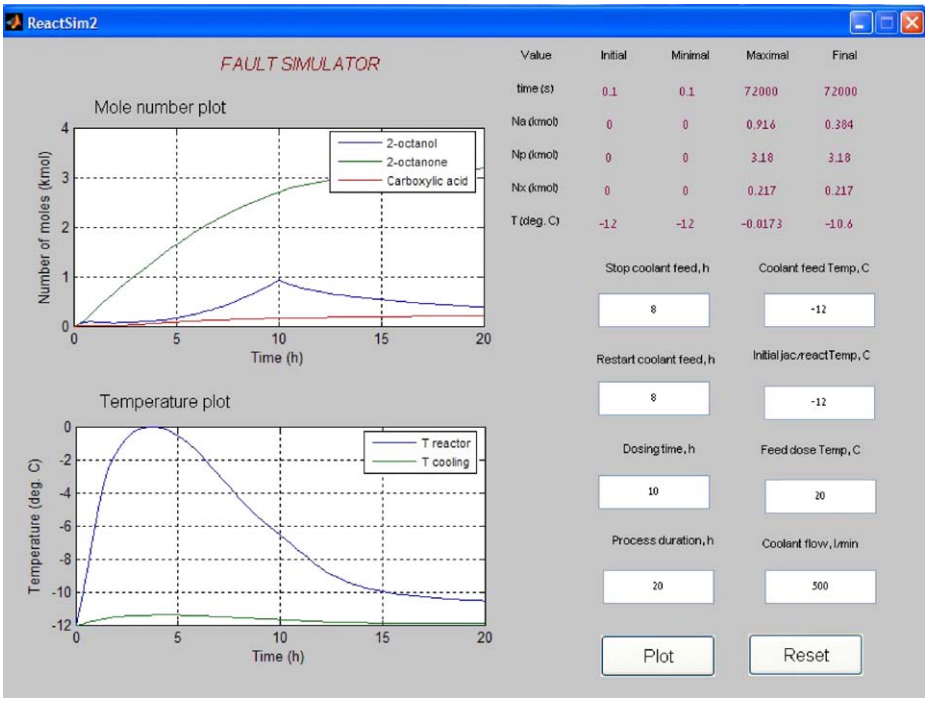

Fig. 3. Graphical user interface for the semi-batch reactor simulation program.

Table 4
Semi-batch reactor operation when the inlet temperature of the cooling media is increased to 265 K (normal value 260 K)

	Variable	Initial value	Minimal value	Maximal value	Final value
1	t (time, s)	0.0001	0.0001	72000	72000
2	N_p (2-octanone, mol)	0	0	1.368575	0.3353062
3	N_x (carboxylic acids, mol)	0	0	2.404981	2.404981
4	T_r (reactor temperature, K)	260	260	410.1594	265.6675
5	T_{cool} (cooling temperature., K)	273.15	265.1546	289.1191	265.1546

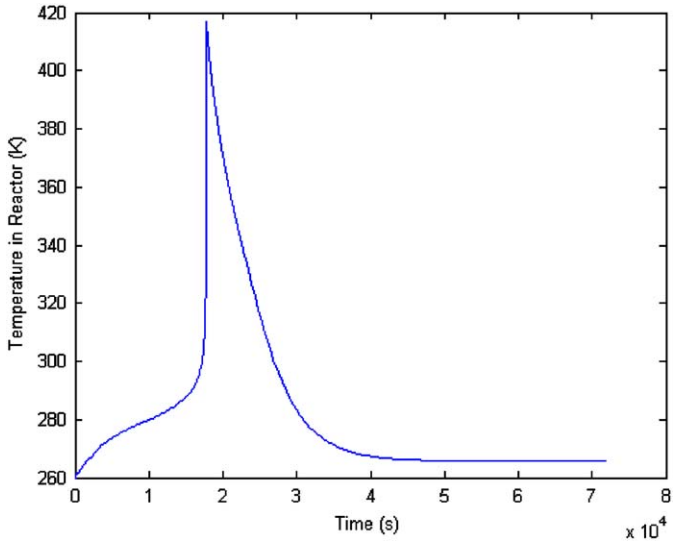

Fig. 4. Temperature variation in the reactor when the inlet temperature of the cooling media is increased to 265 K (normal value 260 K).

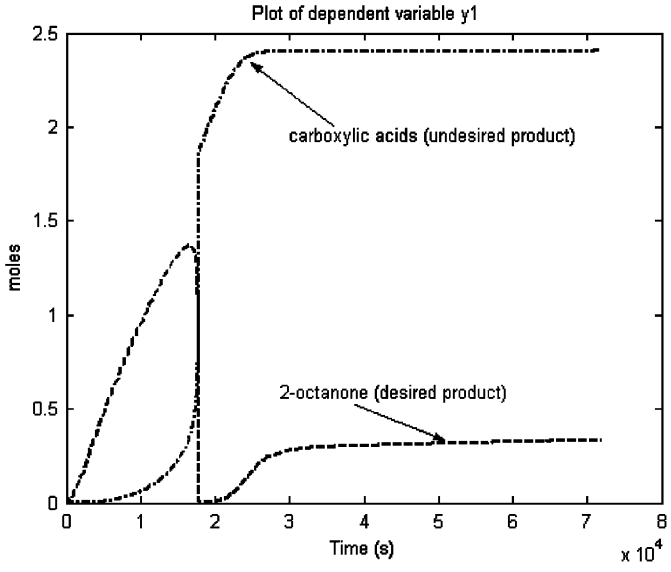

Fig. 5. Molar amounts of the desired and the undesired products when the inlet temperature of the cooling media is increased to 265 K (normal value 260 K).

Table 5
Investigation of the effect of the reduction of the flow rate of the coolant

F_w (l/min)	600	300	200	100	70
n_P (kmol)	3.18	3.17	3.16	3.07	0.01
n_X (kmol)	0.21	0.23	0.26	0.36	3.78
$T_{cool,max}$ (°C)	−11.5	−11.0	−10.4	−8.40	39
$T_{reactor,max}$ (°C)	−0.15	−0.55	1.31	4.38	196

Table 6
Investigation of the effects of the reduction of the effective heat transfer rates

Effective heat transfer rate	100%	90%	81%	80%	70%	60%
n_P (kmol)	3.16	3.08	0.05	0.14	0.3	0.38
n_X (kmol)	0.26	0.33	3.71	3.3	2.63	2.64
$T_{cool,max}$ (°C)	−10.4	−10.2	8.88	6.42	0.3	2.37
$T_{reactor,max}$ (°C)	1.31	3.9	195	177	147	128

Table 7
Some deviations that may cause temperature runaway

Guide word	Deviation	Normal value	Limit
None	No flow in the cooling jacket		
Less of	Lower coolant flow-rate	600 l/min	Less than 70 l/min
Less of	Smaller heat transfer area	100%	Less than 81%
More of	Higher coolant temperature	−15	More than −6
Less	Shorter dosing time	20 h	Less than 7.5 h
More of	Larger dosing volume	0.6 m^3	More than 0.81 m^3
More of	Higher nitric acid concentration	59%	More than 64%

the effective heat transfer rate gets below 81% of the design value temperature runaway develops, where $T_{r,max} = 195\,^{\circ}C$. Such extreme consequences of a relatively small reduction of the effective heat transfer rate indicate that the safety margin on the heat transfer area is not large enough. This may suggest changes in the reactor design to increase the heat transfer area (by adding an internal cooling coil, for example).

In Table 7, some of the deviations that may cause temperature runaway are shown. It includes, also, the normal value and the safe operation limit value for the different variables. In some cases the range of the safe operation is quite wide (like in the case of the coolant flow rate), while in the others, there is only a narrow range of safe operation (higher nitric acid concentration, for example). In the latter cases, changes in the reactor design should be considered in order to widen the range of safe operation.

5. Discussion and conclusions

A quantitative HAZOP procedure well suited for educational and operator training purposes has been developed. The use of this procedure has been demonstrated by applying it to a semi-batch reactor in which an exothermic reaction is carried out (van Woezik & Westerterp, 2001). The basic model of the reactor was developed using the Polymath 6.1 mathematical software package. Upon verifying the correctness of the model, it was exported to MATLAB and a graphical interface was added to make the dynamic simulation program suitable for educational and training applications. Using the quantitative HAZOP procedure, the possible process deviations were examined and practical threshold values on the process deviations were determined. Exceeding those threshold values may lead to temperature runaway in the reactor. It was shown that in some cases the design of the reactor must be changed in order to extend the reactors' normal operability range.

It should be pointed out that quantitative HAZOP complements the traditional HAZOP procedure, does not replace it. There are still many processes that cannot be modeled for the lack of enough quantitative information, particularly in emergency situations. Thus, the quantitative version needs to be taught and used with the standard HAZOP procedure.

The various programs that were used for carrying out the quantitative HAZOP for the process of the oxidation of 2-octanol in a semi-batch reactor are available at: ftp://ftp.bgu.ac.il/shacham/OctanoneProd/. The use of those programs can enhance considerably the safety education by providing tools for systematic screening of process deviation for possible hazardous events, determining the threshold values that may lead to such events and enabling the examination of a particular design for satisfactory range of safe operation.

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