Prediction and Prevention of Chemical Reaction Hazards – Learning by Simulation

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Abstract

Assignments based on dynamic simulation of a batch reactor and a semi-batch reactor in which exothermic reactions are conducted, are used to teach students the various aspects of process safety. The students can observe temperature runaway taking place because of incidents, such as overcharging, cooling water failure, pipe blockage and excessive initial heating. They can derive various strategies to prevent temperature runaway developing as the result of such incidents and suggest operational and structural changes of the process to make it more resilient to component failures and incidents.

Introduction

Learning to predict and to prevent chemical process hazards is an essential part of the chemical engineer's education. In addition to courses specially dedicated to process safety engineering this subject should also be incorporated into existing chemical engineering courses such as design, reaction kinetics and thermodynamics [1]. The emphasis put on safety in the various courses makes it clear to the students that safety considerations are essential components of process and equipment design and operations.

Learning by simulation is very effective since the student has the chance to "discover" for himself the consequences of failure of critical components or operators' mistakes. Simulation also enables the student to suggest and try various strategies dealing with the emergency situation and rapidly investigate the effectiveness of these strategies in preventing culmination of component failures into serious accidents.

A major cause of accidents in the chemical industry are runaway reactions and, as Mannan *et al*.[1] pointed out, no course in reaction engineering is complete without due treatment of runaway reactions. We have developed two examples of exothermic reactor simulation that can be used for investigation of the effects of some of the common, documented causes of accidents involving thermal runaway reactions. These examples can be given as homework assignments in undergraduate courses, such as "Reaction Engineering" or

Example 1. Propylene oxide polymerization in a semi batch reactor

Propylene oxide polymerization is a highly exothermic process, which is carried out at high pressures. Nearly isothermal operation is required in order to

prevent runaway conditions and the buildup of a pressure exceeding, the reactor design pressure. Safety problems associated with the operation of such a reactor are described in Kneale and Foster [2]. Mathematical modeling and simulation of the reactor, which includes a burst-disk for pressure relief in case of excessive pressure buildup, was carried out by Ingham *et al*. [3].

Catalyzed butanol is initially charged into the reactor. Propylene oxide is fed into the reactor at a constant rate until the batch is ready and the reactor is full. Excess heat of the reaction is removed via an external heat removal system. Economical considerations dictate that the reaction should be completed at the highest possible rate. The reaction rate is a function of the temperature, catalyst concentration and liquid phase oxide concentration (which is function of the pressure). The limits on the reactor temperature and catalyst concentration are set by considerations of thermal degradation and purification difficulties. To maximize the reaction rate, the pressure must be kept as high as possible for the entire duration of the batch. The higher limits on the pressure and reaction rate are dictated by the pressure suitability of the reactor system and the feasible heat removal rate.

As part of the assignment involving this example the students are usually provided with the mathematical model of the process (as presented by Ingham *et al*.[3]) operating in normal operating conditions. The model of the reactor, the heat removal system and the burst-disk orifice is shown in (tab. 1) in a format compatible with POLYMATH 5.0[a] numerical computation package. Note that other computation packages (such as for example Maple[b] and MATLAB[c]) can as well be used for solving the system of ODE representing the semi-batch process. The table was prepared using the EXCEL[d] spreadsheet program, taking advantage of its database management options that are needed for the construction of a flexible process model.

To run a simulation of the reactor under normal operating conditions, the 'Model equations' column in (tab. 1) should be saved as an ASCII (text) file. POLYMATH can read and execute this file, but some modifications of this file will be needed if other numerical solver is used. The information included in (tab. 1) enables the student 1. To fully understand the mathematical model of the process, 2. To run the simulation of the base case without doing any programming or other technical effort unrelated to the subject matter, and 3. Modify the model easily for carrying out hazard and operability analysis.

A typical student assignment includes verification of the model by carrying out the simulation in normal operating conditions and comparing results with the solution provided by the instructor. Then, checking the effects of reducing the cooling re-circulation (from 5000 kg/min to 4300 kg/min and to 4200 kg/min), of cooling water failure of a varying duration at different stages of the batch, of

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cooling pipe blockage and of failure of the bursting disk to open at the specified rupture pressure (8 bar). If temperature runaway (reactor pressure exceeds the 8 bar limit) is due to happen in any of those cases, the students are also asked to suggest changes in the operating conditions that may enable a successful completion of the batch.

In normal operating conditions the temperature changes are quite moderate. After about 13 h, the temperature reaches a maximal value of 112 ºC. At this point the increased reaction rate, associated with the high temperature (and pressure), reduces the oxide concentration. This, in turn, affects a reduction of the reaction rate (and the temperature) until the trend is reversed again, showing increasing reactor temperature. The change of pressure presents a similar trend, the highest pressure reached (6.35 bar) is well below the bursting pressure. The batch is completed after 33 h and 20 min and the molecular weight of the final product is MW=2895.

If the cooling re-circulation is reduced to 4200 kg/min, runaway conditions develop after about 13 hours of operation. The temperature reaches 230 ºC, the pressure reaches the threshold value of 8 bar and the burst disk is ruptured. At this point, the feed of the propylene oxide is stopped and the reaction rate is reduced to zero due to the diminishing oxide concentration. The molecular weight of the product in this case is 1818, which is far from the specifications. Temperature runaway can be prevented in this case by, for example, increasing the cooling circulation rate to 5000 kg/min once the temperature in the reactor exceeds 110 ºC.

A conclusion to be drawn from this simulation study is that this process is highly resilient to a single failure or incident due to the excessive cooling capacity and the use of a semi-batch reactor. By reducing the feed rate of the propylene oxide and/or increasing the cooling circulation rate temperature runaway can be prevented.

Example 2. A batch reactor with consecutive reactions (Luyben[4]).

This example involves a batch reactor in which the exothermic liquid-phase reaction A B C is carried out. After the reactant is charged into the vessel, steam is fed into the jacket to heat the reaction mass up to the desired temperature. Thereafter, cooling water is fed into the jacket to remove the exothermic heat of reaction and to make the reactor follow a prescribed temperature-time curve. The objective is to maximize the production of the desired product, B.

The equations describing the operation of the reactor at the various stages are shown on pages 150-157 in Luyben[4]. The simulation model of this reactor is much more complex than that of the semi-batch reactor and it is not included here. Complete details of the model are provided by Shacham *et al*. [5]. As in the previous example students are usually provided with the mathematical model of the process operating in normal operating condition in a format compatible with the POLYMATH 5.0 numerical computation package.

The student assignments are similar to those given in the previous example, as well as checking effects of overcharging (by increasing the initial concentration of the reactant) and failure to control duration of steam heating. If temperature runaway is due to happen in any of those events, the students are asked to suggest changes in the operating conditions that may enable a successful completion of the batch.

In normal operating conditions, the temperature in the reactor increases steadily during the steam heating. It reaches its maximum short time after the heating is turned off and cooling is turned on and decreases gradually until the end of the batch with 60% conversion of the reactant to the desired product. However, with about 20% overcharging, runaway conditions develop as the temperature keeps increasing even after the cooling is turned on. In some of the incidents included in the assignment, development of runaway conditions can be prevented and the batch can be completed successfully by shortening the steam heating period and increasing the cooling water flow rate. However, the general conclusion to be drawn in view of the simulation results is that the resilience of this process to even a single component failure is very low. To increase its resilience the heat transfer area of the cooling system must be significantly increased.

Conclusions

The small scale and flexible process simulators suggested in this study can be effectively used in an educational environment for investigation of process behavior and identification of the influential variables in emergency conditions. The influential variables are the ones that should be manipulated in order to prevent the culmination of a component failure into a major accident. Using simulation, the common causes of incidents in the chemical industry can be checked for their relevance in the process being studied.

It should be emphasized that model validation is usually based on process data taken under normal operating conditions. Verification of the simulation results under emergency conditions is rather difficult because process data in such conditions is rarely available. Therefore, the model assumptions must be carefully checked for their validity in emergency conditions.

Literature

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Table 1: Model Equations and Output Variable Description for Example 1

Output variable

No.	Name	Definition	Initial value	Model equations - Runaway polymerization reaction
1	M	Total mass in the reactor (kg)	M(0)=4400	d(M)/d(t) = F-V
2	MC	Oxide mass in the reactor (kg)	MC(0)=0	d(MC)/d(t) = F-V-r
3	TR	Temperature in the reactor (° C)	TR(0)=80	d(TR)/d(t) =(Hc-Hv-Qg-Qr)/(M*Cp)

4	X	The mass of oxide reacted (kg)	X(0)=0	d(X)/d(t) = r
5	Open	Status of the burst disk: 0 closed, >0	Open(0)=0	d(Open)/d(t) = if (P<Pburst) then (0) else (0.001)
6	F	Oxide feed rate (kg/min)		F = if (Open>0) then (0) else (100)
7	V	Vapor discharge rate (kg/min)		V = if ((P<=1) or (Open==0)) then (0) else (V1)
8	V1	Vapor discharge rate (kg/min)		V1 = if (P<1.9) then (Vsubs) else (Vs)
9	Vs	Sonic vapor discharge rate (kg/min)		Vs=0.85*Kv*P/sqrt(TR+273)
10	Vsubs	Sub-sonic - vapor discharge rate (kg/min)		Vsubs=Kv*P/sqrt((TR+273))*sqrt(1+1/P^2)
11	r	Reaction rate (kg oxide/min)		r = k*MC
12	Hc	Feed enthalpy change (kJ/min)		Hc= F*Cp*(T0-TR)
13	Hv	Latent heat of vapor discharge (kJ/min)		Hv=V*Lamda
14	Qg	Heat of reaction (kJ/min)		Qg=r*HR
15	Qr	Heat removal (kJ/min)		Qr=Fc*Cp*(TR-T0)
16	P	Oxide vapor pressure (bar)		P = if (P1<1) then (1) else (P1)
17	P1	Oxide vapor pressure (bar)		P1 = (exp(-3430/(TR+273)+11.7)+1.45e-3*MW)*C
18	k	Reaction rate coefficient		k = 9e9*exp(-E/(R*(TR+273)))
19	C	Oxide concentration (kg/kg)		C = MC/M
20	MW	Molecular weight of the polymer (kg/mol)		MW = (M0+X)/(M0/74)
21	T0	Feed temperature (ºC)		T0 = 80
22	Lamda	Heat of vaporization of the oxide (kj/kg)		Lamda = 670
23	Cp	Spec. heat of feed reacting mass (kJ/kg- º C)		Cp = 3.5
24	HR	Heat of reaction (kJ/ kg oxide)		HR = -1660
25	Fc	Re-circulation mss flow rate (kg/min)		Fc = 3300
26	Pburst	Disk rupture pressure (bar)		Pburst = 8
27	R	Gas constant		R = 1.987
28	E	Activation energy		E = 21000
29	M0	Initial alcohol charge (kg)		M0 = 4400
30	Kv	Valve discharge coefficient		Kv = 100