The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and that elucidate difficult concepts. Manuscripts should not exceed ten double-spaced pages if possible and should be accompanied by the originals of any figures or photographs. Please submit them to Professor James O. Wilkes (e-mail: wilkes@umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

PREDICTION AND PREVENTION OF CHEMICAL REACTION HAZARDS

Learning by Simulation

Mordechai Shacham
Ben Gurion University of the Negev • Beer-Sheva 84105, Israel
Neima Brauner
Tel-Aviv University • Tel-Aviv 699 78, Israel
Michael B. Cutlip
University of Connecticut • Storrs, CT 06269

Learning to predict and prevent chemical process hazards is an essential part of the chemical engineer's education. Mannan, *et al.*,[1] 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 large. Mannan, *et al.*,[1] for example, quote a study that found that more than 34,500 accidents involving toxic chemicals occurred over a period of five years (1988-1992) in the U.S. Recently there have been many requests to develop standards for reducing the frequency and severity of chemical accidents. The university obviously plays a critical role in achieving this objective.

Mannan, *et al.*,[1] suggest that students should take specific courses on process safety engineering. Process safety should also be incorporated into existing chemical engineering courses, such as design, reaction kinetics, and thermodynamics. The objective of putting such great emphasis on safety issues is to ensure that safety will become second nature for the engineer. It is important to make it clear to students that safety considerations are essential components of the design and operation of process equipment.

Learning by simulation is very effective since students have the chance to discover for themselves the consequences

Mordechai Shacham *received his BSc (1969) and his DSc (1973) from Technion, Israel Institute of Technology. He is a professor of chemical engineering at the Ben-Gurion University of the Negev, Beer-Sheva, Israel, where he has served since 1974 at every academic level, including two four-year terms as department head. His research interests include analysis, modeling, regression of data, applied numerical methods, computer-aided instruction, and process simulation, design, and optimization.*

Neima Brauner *is professor and head of mechanical engineering undergraduate studies in the Department of Fluid Mechanics and Heat Transfer at Tel-Aviv University, Tel-Aviv, Israel. She received her BSc and MSc in chemical engineering from the Technion Israel Institute of Technology, Haifa, Israel, and her PhD in mechanical engineering from Tel-Aviv University. Her research has focused on the field of hydrodynamics and transport phenomena in two-phase flow systems.*

Michael B. Cutlip *is a BS and MS graduate of The Ohio State University (1964) and a PhD graduate of the University of Colorado (1968), all in chemical engineering. He is the immediate past chair of the Chemical Engineering Division of the ASEE and is cochair of the Division's Summer School for Chemical Engineering Faculty to be held in 2002. He is a coauthor with Mordechai Shacham of the POLYMATH software package and a recent textbook on numerical problem solving.*

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of operator mistakes or of failure of a critical component. Simulation also enables students to consider various strategies for dealing with the emergency situation and then to rapidly investigate the effectiveness of these strategies in preventing culmination of the component's failure into a serious accident.

Chemical reaction hazards are a major cause of accidents in the chemical industry,[2] and thermal runaway reactions are probably responsible for most of those accidents. Therefore, no course in reaction engineering is complete without due treatment of runaway reactions.[1] To fully understand the various aspects involved in safety of exothermic reactions, issues related to the cooling and control systems must also be discussed. A realistic model of a cooled exothermic reaction can be, however, too involved and complex to be discussed in depth in a particular course.

In order to solve this dilemma, we have selected a model described in detail in a textbook.[3] The course instructor can describe parts of the model relevant to the course and refer the students to the textbook for a detailed description of the additional subjects. The batch reactor model presented by Luyben[3] and the simulation technique described by Shacham, *et al.*,[4] are used in this paper to derive a simulation exercise that allows students to investigate prime causes of incidents involving runaway reactors. The potential causes that can be investigated using this simulator include, for example, overcharging, failure to control steam pressure or duration of steam heating, the loss of cooling water, and pipe blockage.

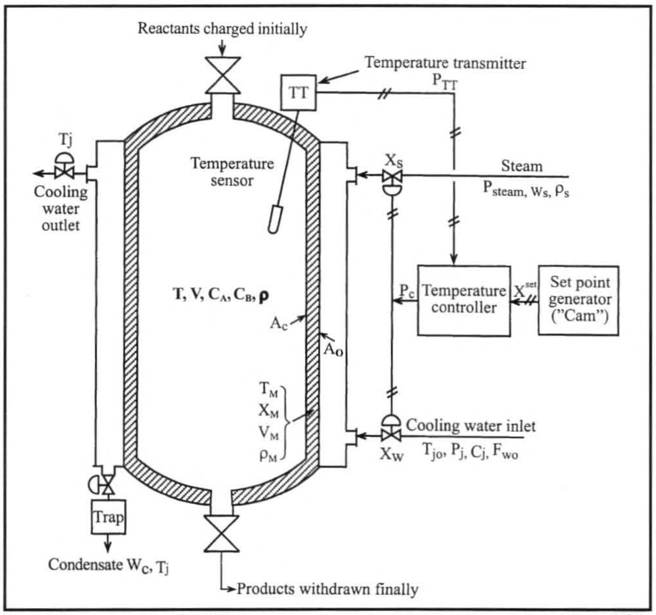

Figure 1. *Cooled batch reactor (based on Luyben[3]).*

In order to investigate the various options, the student should be able to follow and understand the fairly complex simulation model in the form used for presentation to a numerical solver for solution. In the past, FORTRAN programs—which are difficult to follow and understand—had to be used for simulation (see Luyben[3]). The currently available software packages, however, such as Maple,[5] MATLAB,[6] and POLYMATH,[7] make it possible to present the simulation model in an almost mathematical form—which is easy to follow and understand.

PROBLEM STATEMENT

The exothermic liquid-phase reaction A→B→C is carried out in a batch reactor, which is sketched in Figure 1.

After the reactant is charged into the vessel, steam is fed into the jacket to heat the reaction mass 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 (various hydrogenation and nitration reactions can serve as typical examples for such a sequence of reactions).

The equations describing the operation of the reactor at the various stages are summarized in Table 1, Parts 1 and 2, (see next page). For further explanation, the reader is referred to the problem definition in Luyben,[3] pages 51-62 and 150-157, where the equations are shown in their mathematical form. The corresponding equation numbers are shown in the second column of Table 1. The format of the equations presented in Table 1 is that required by POLYMATH© 5.0 Numerical Computation Package.

The mass and energy conservation equations for the reacting liquid and the vessel metal are given in rows 1-5 of Table 1. The equations for the heating/cooling jacket are different for the various phases of the batch. The first phase involves heating with steam at a supply pressure given by *Psteam*. The corresponding equations describing the temperature (and additional variables) inside the jacket are shown in rows 7-14 of Table 1. Note that the calculation of the temperature inside the jacket involves solution of a differential algebraic system of equations (DAE). The "controlled integration" method of Shacham, *et al.,*[8] is used for solving this DAE. A detailed explanation on the use of the controlled integration method for this particular problem can be found in this reference.[8]

Steam heating lasts until the temperature, denoted as *Theatmax,* is reached inside the reactor. At this point the steam heating is switched off and the flow of cooling water into the jacket is turned on. This is governed by the variable *cooling* (see row 6 in Table 1), which initially is positive and keeps increasing as long as the temperature inside the reactor is greater than *Theatmax*. Thus it is always positive throughout the cooling period.

The equations representing the cooling-water-flow rate, water volume in the jacket, and heat transfer are shown in rows 15-17 of Table 1. The equation for calculating the

TABLE 1

Part 1

Definition of the Equations and Output Variables for the Batch Reactor Problem

		Output variable		Definition	Description
No.	No. in Book	Name	Initial value	Exothermic Reactions in a Batch Reactor|POLVER05_0	
1	5.35	Ca	Ca(0)=0.8	d(Ca)/d(t) = -k1*Ca	Concentration of A (mol/cu. ft.)
2	5.36	Cb	Cb(0)=0	d(Cb)/d(t) = k1*Ca-k2*Cb	Concentration of B (mol/cu. ft.)
3	5.37	T	T(0)=80	d(T)/d(t) = (-HR1*k1*Ca-HR2*k2*Cb)/rho-Qm/(rho*V)	Temperature in the reactor vessel (deg. F)
4	5.38	Qm		Qm = hi*A0m*(T-Tm)/60	Heat transferred through the metal wall (Btu/min)
5	5.39	Tm	Tm(0)=80	d(Tm)/d(t) = (Qm-Qj)/(rhom*Cpm*Vm)	Temperature of the metal wall (deg. F)
6		Cooling	Cooling(0)=0	d(Cooling)/d(t) = if (T<Theatmax) then (0) else (0.001)	Jacket's operational status (0 heating, >0 cooling)
7	5.40	rhos	rhos(0)=0.0803	d(rhos)/d(t) = if (Cooling==0) then (ws-wc)/Vjmax else (0)	Density of the steam in the jacket (lb/cu. ft.)
8	new and 5.51	Tj	Tj(0)=259	d(Tj)/d(t) = if (Cooling==0) then (Kc*(err+drhosdt/10)) else (((Fw0*(Tinj-Tj)+Qj/rhoj)/Vj))	Temperature in the heating/cooling jacket(deg. F)
9	5.41	err		err = rhos-18*144*Pj/(1545*(Tj+460))	Steam density deviation for controlled integration
10	5.42	Pj		Pj = exp(15.70036-8744.4/(Tj+460))	Steam pressure inside the jacket (psi)
11	5.43	ws		ws = if (Pj>Psteam) then (0) else (xs*Cvs*sqrt(Psteam-Pj))	Steam mass flow rate (lb/min)
12	5.44 and 5.49	Qj		Qj = if (Cooling==0) then (-hos*Ajmax*(Tj-Tm)/60) else (how*A0*(Tm-Tj)/60)	Heat transferred to the jacket (Btu/min)
13	5.45	wc		wc = -Qj/Hvap	Condensate mass flow rate (lb/min)
14	New	drhosdt		drhosdt = (ws-wc)/Vjmax	Steam density derivative (for controlled integration)
15	5.46	A0		A0 = Vj*Ajmax/Vjmax	Heat transfer area for cooling (cu. ft.)
16	5.47	Vj	Vj(0)=0.001	d(Vj)/d(t) = if (Cooling>0 and Vj<Vjmax) then (Fw0) else (0)	Volume of cooling water in the jacket (cu. ft.)
17	5.50	Fw0		Fw0 = if (Cooling>0) then (Cvw*sqrt(Wp)*8.33*xw/rhoj) else (0)	Cooling water mass flow rate (lb/min)
18	5.52	Ptt		Ptt = 3+(T-50)*12/200	Output pneumatic signal from temp. transmit. (psi)
19	5.53	P1		P1 = 7+2*(Pset-Ptt)	Controller output pressure (psi)
20	5.53	Pc		Pc = if (P1<3) then (3) else (if (P1>15) then (15) else (P1))	Controller adjusted output pressure (psi)
21	5.54	Pset	Pset(0)=12.6	d(Pset)/d(t) = if (Cooling>0) then (RAMP) else (0)	Set point signal (psi)
22	see p. 151	x1		x1 = (Pc-9)/6	Steam valve - fraction open
23	see p. 151	xs		xs = if (x1<0) then (0) else (if (x1>1) then (1) else (x1))	Steam valve - fraction open (adjusted)
24	see p. 151	xw1		xw1 = (9-Pc)/6	Cooling water valve - fraction open
25	see p. 151	xw		xw = if (xw1<0) then (0) else (if (xw1>1) then (1) else (xw1))	Cooling water valve - fraction open (adjusted)
26	3.63	k1		k1 = 729.5488*exp(-15000/(1.99*(T+460)))	Reaction rate coefficient for A -> B (1/min)
27	3.63	k2		k2 = 6567.587*exp(-20000/((T+460)*1.99))	Reaction rate coefficient for B -> C (1/min)

Part 2

Definition of Constants for the Batch Reactor Problem

No	Source	Name		Definition	Description
28	Table 5.12	HR1		HR1 = -40000	Heat of reaction for A -> B (Btu/mol)
29	Table 5.12	HR2		HR2 = -50000	Heat of reaction for B -> C (Btu/mol)
30	Table 5.12	rho		rho = 50	Density of reacting mass (lb/cu.ft.)
31	Table 5.12	V		V = 42.4	Volume of reaction vessel (cu. ft.)
32	Table 5.12	rhom		rhom = 512	Density of metal wall (lb/cu.ft.)
33	Table 5.12	Cpm		Cpm = 0.12	Specific heat of metal wall (Btu/lb.- cu. ft.)
34	Table 5.12	Vm		Vm =9.42	Volume of metal wall (cu. ft.)
35	Table 5.12	rhoj		rhoj = 62.3	Density of cooling water (lb/cu.ft.)
36	Table 5.12	Tinj		Tinj = 80	Cooling water inlet temperature (deg. F)
37	FORTRAN progr.	Theamax		Theatmax = 200	Temperature for switching from heating to cooling (deg. F)
38	Table 5.12	Vjmax		Vjmax = 18.83	Total volume of the jacket (cu. ft.)
39	FORTRAN progr.	RAMP		RAMP = -0.0005	Rate of Pset change with time (psi/min)
40	Table 5.12	hi		hi = 160	Inside heat transfer coeff. (Btu/hr-deg. F-cu. ft.)
41	Table 5.12	A0m		A0m = 56.5	Metal heat transfer area (cu. ft.)
42	Table 5.12	Ajmax		Ajmax = 56.5	Jacket's total heat transfer area (cu. ft.)
43	Table 5.12	hos		hos = 1000	Jacket's heat transfer coeff. (with steam, Btu/hr-deg. F-cu. ft.)
44	Table 5.12	how		how = 400	Jacket's heat transfer coeff. (with water, Btu/hr-deg. F-cu. ft.)
45	Table 5.12	Hvap		Hvap = 939	Steam's heat of condensation (Btu/lb)
46		Kc		Kc = 7000	Proportional gain for controlled integration
47	FORTRAN progr.	Psteam		Psteam = 35	Steam's supply pressure (psi)
48	Table 5.12	Cvs		Cvs =112	Steam valve's coefficient (lb/min - sqrt(psi))
49	Table 5.12	Cvw		Cvw = 100	Water valve's coefficient (gpm/sqrt(psi))
50	FORTRAN progr.	Wp		Wp = 20	Water header pressure (psi)

water temperature in the jacket is given in row 8. The equations related to the control system—namely the output (pneumatic pressure) signal from the temperature transmitter, the controller's output pressure, the set-point signal, and the fractional openings of the steam and water valves—are shown in rows 18-25 of Table 1.

The Arrhenius equations describing the change of the reaction rate coefficients as functions of the temperature in the reactor are shown in rows 26-27 and the numerical values of the various constants are defined in rows 28-50.

TYPICAL STUDENT ASSIGNMENTS

1. Simulate the normal operation of the batch reactor by solving the model described in Table 1, which also shows all the parameters and initial values. The reaction duration is two hours and forty minutes. Verify the correctness of your solution by comparing your results with those shown in Table 2 and Figure 2. Note that if POLYMATH 5.0 is used to solve the model, the equations, the constant definitions, and the initial values of the variables can be "copied" from Table 1 and "pasted" into POLYMATH 5.0. If another program is used, Maple or MATHLAB for example, the equations must be rewritten in the syntax and format required by the particular program.
2. Check the effects of overcharging. Change the initial concentration of component A to C_{a0}=1.0 lb mole/ft^3 (instead of C_{a0}=0.8 lb mole/ft^3 in normal operation). Note that the reaction vessel can withstand a pressure of up to 1,600 psi, which is reached when the temperature in the reactor approaches 500°F. If overcharging results in a temperature runaway, suggest changes of the operating conditions that will enable successful completion of the batch.

TABLE 2
Batch Reactor Simulation Results for Normal Operating Conditions*

Name	Initial value	Minimal value	Maximal value	Final value
time	0	0	160	160
Ca	0.8	0.2534251	0.8	0.2534251
Cb	0	0	0.4797339	0.4797339
T	80	80	211.70419	193.23402
Qm	0	0	1.32E+04	4345.6661
Tm	80	80	164.3911	164.3911
Tj	259	89.494809	259	151.91749
Pj	34.414173	0.8065525	34.414173	4.0967667
Qj	-168600	-168600	21170	4698.481
xs	1	0	1	0
ws	85.72406	0	85.72406	0
xw	0	0	0.3701784	0.0224042
Fw0	0	0	22.135179	1.3396817
k1	6.32E-04	6.32E-04	0.0097696	0.0071075
k2	5.43E-05	5.43E-05	0.0020885	0.0013665

** The solution is reported using an excessive number of digits for the stage of model and numerical solver validation.*

3. Check the effects of failure to control duration of steam heating. Change *Theatmax* (the temperature in the reactor when the switch from heating to cooling takes place) to 220°F and to 230°F (instead of the normal value of 200°F). If this causes temperature runaway, suggest changes of the operating conditions needed for completing the batch successfully.
4. Check the effects of pipe blockage. Change the value of *Wp* (water header pressure) to 10 psi to simulate an extra drop in pressure because of pipe blockage. If this causes temperature runaway, suggest changes of the operating conditions that will enable successful completion of the batch.
5. Check the effects of cooling water failure. Set the value of *Fw0* to zero starting at a point two hours after the start of the batch and lasting until its completion. Does this cause a temperature runaway? Check the effects of cooling water failures of various durations at various stages of the batch.
6. Discuss the flexibility of the batch reactor system to operate in emergency conditions and suggest ways to increase the system resilience.

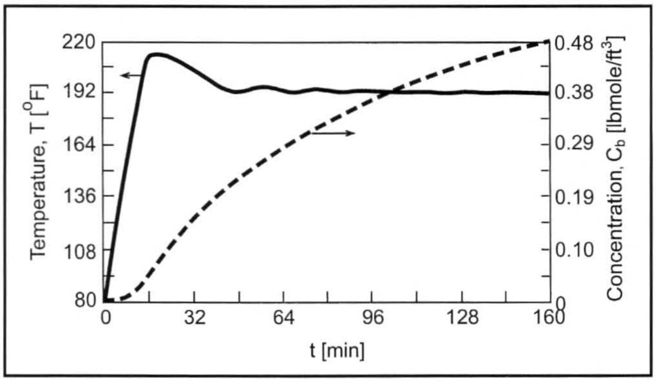

***Figure 2.** Variation of the temperature and the concentration of the desired product (C_b) in the reactor (normal operating conditions).*

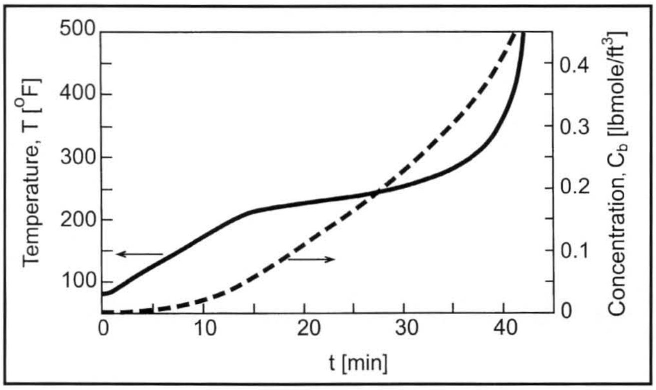

***Figure 3.** Variation of the temperature and C_b in the reactor when reactant concentration is increased to C_{a0}=1.0 lb mole/ft^3.*

EXPECTED SIMULATION SOLUTIONS

1. Normal operating conditions

The initial, minimal, maximal, and final values of the principal variables are shown in Table 2. The maximal concentration of the desired product B is 0.48 lb mole/ft^3, meaning sixty percent of the reactant A is converted to B. The highest temperature in the reactor is 211.7°F, well inside the safe region. It is interesting to note that the maximal opening of the cooling water valve (xw) is only 37%, meaning there is some excess capacity in the cooling water system. Figure 2 shows the variation of the temperature and the concentration of B in the reactor. The temperature increases steadily during the steam heating. It reaches its maximum a short time after the heating is turned off and cooling is turned on. From that point, it decreases gradually throughout the duration of the reaction.

2. Overcharging

To simulate overcharging, the initial concentration of A is set to 1.0 lb mole/ft^3. Figure 3 shows the variation of the temperature and concentration of B in the reactor for this case. Note that the temperature keeps increasing even after the cooling is turned on. The increase is gradual at first, but after about 35 minutes, runaway conditions develop. The temperature reaches the threshold limit of 500°F at 42 minutes after the start of the batch.

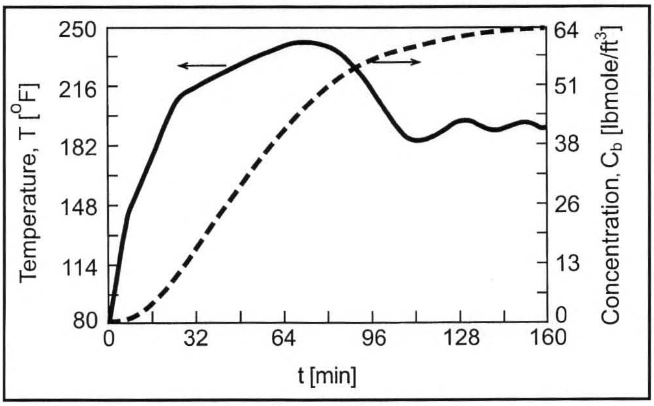

Figure 4. *Variation of the temperature and C_b in the reactor when reactant concentration is increased and heating period duration is decreased.*

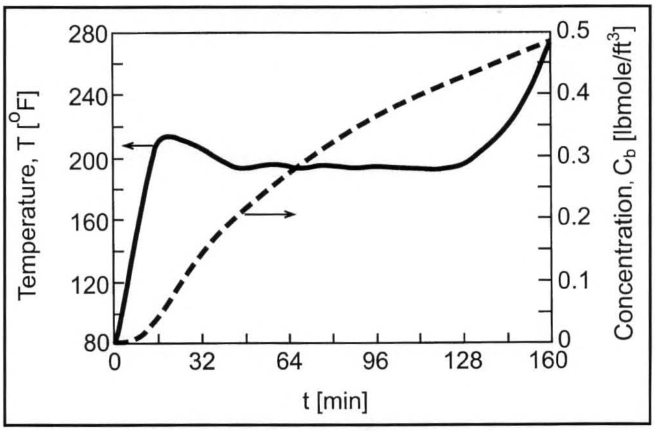

Figure 5. *Variation of the temperature and C_b in the reactor when cooling water fails after two hours of operation.*

Shortening the duration of the steam heating period can prevent temperature runaway in this case. The variation of the temperature and concentration of B in the reactor when *Theatmax* is set to 125°F is shown in Figure 4. The temperature rise continues long after the heating is turned off, reaching a maximal value of 241°F. At this point, however, the concentration of A is low enough so that the cooling system is able to remove the excess reaction heat and prevent temperature runaway. The final concentration of B is 0.637 lb mole/ft^3, meaning 63.7% of the reactant, A, is converted to the desired product, B. In this case the reactor's performance is even slightly better than under normal operating conditions.

3. Failure to control duration of steam heating

If the switch from heating to cooling takes place when the temperature in the reactor reaches 220°F (set *Theatmax*=220), the extra cooling capacity of the system is able to remove the excess of reaction heat and temperature runaway is prevented. The maximal opening of the cooling water valve is 83%, the maximal temperature is 234°F, and the final concentration of B is 0.625 lb mole/ft^3—thus the batch is completed successfully. If switching from heating to cooling is done when the temperature in the reactor reaches 230°F, however, runaway conditions develop after about 55 minutes and the threshold value of 500°F is reached about one hour after the start of the batch. Prevention of temperature runaway in this case requires structural changes in the cooling system. Doubling the heat transfer area, for example, enables successful completion of the batch even with *Theatmax*=230.

4. Pipe blockage in the cooling system

Because of the extra cooling capacity of the system, reduction of the effective water header pressure by fifty percent (brought about by pipe blockage) has very little effect on the temperature trajectory of the batch. The maximal temperature increases to 215°F, but there are no other noticeable differences from normal operating conditions. The maximal water valve opening is still only 46%. This means the cooling system extra capacity can accommodate an even more serious pipe blockage.

5. Cooling water failure

Cooling water failure can be implemented in the model (shown in Table 1) by introducing a new variable: *fail*=1, if there is cooling water failure, and *fail*=0 otherwise. The equation for calculating *Fw0* (Eq. 17 in Table 2) must also be changed by multiplying it by (1-*fail*).

Figure 5 shows the variation of the temperature and concentration of B in the reactor for the case where the cooling water system fails two hours after the start of the batch and is not recovered until the end of the batch. While the temperature increases considerably (final temperature is 278°F instead of the normal value of 193°F), it is still far from the dangerous level of 500°F. The concentration of the desired product B is 0.495 lb mole/ft^3, slightly higher than the normal value of 0.479 lb mole/ft^3.

The effect of cooling water failure depends very much on the timing and duration of this event. Even 25 minutes loss of cooling, for example, causes the development of runaway conditions if failure occurs during the first hour of the batch.

DISCUSSION AND CONCLUSIONS

This simulation exercise was given as a homework assignment to the students in the process simulation course at Ben-Gurion University of the Negev. Graduate and senior undergraduate students who have previously studied both chemical reaction engineering and process control normally take this course. These students were asked to complete the assignment in two weeks and most of them did so successfully. They thought the assignment was challenging and interesting and said it helped them better understand the safety-related issues of reactor design. They discovered that increasing the heat transfer area of the cooling system (adding an internal cooling coil to the existing jacket, for example) could increase the resilience of the reactor.

The batch reactor simulation can, of course, be used for demonstrating various effects of additional types of failures, but can also be used for raising some dilemmas that concern the interrelation between economics and safety. In this case, for example, economical considerations dictate fixing the set point of the cooling water controller at the highest possible value in order to achieve a maximal yield of the desired product B. This reduces the safety resilience of the system to a minimum, however.

Additional realistic safety-related simulation exercises can be found in Shacham, *et al.*,[4] where a propylene polymerization reactor is analyzed, and in Fogler,[9] where the "nitroanaline reactor rupture" incident (Sauget, IL, 1969) is modeled.

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