Web Example 13: Synthron Runaway Reaction LEP

The second order polymerization reaction of n-butyl acrylate to synthesize Modarez MFP-BH, a poly-acrylic additive which improves the flow and spreading of various paints and varnishes, was a commonplace reaction in the North Carolina Synthron facility. The reaction was carried out in a semibatch reactor, which is shown schematically below in Figure W13-1.

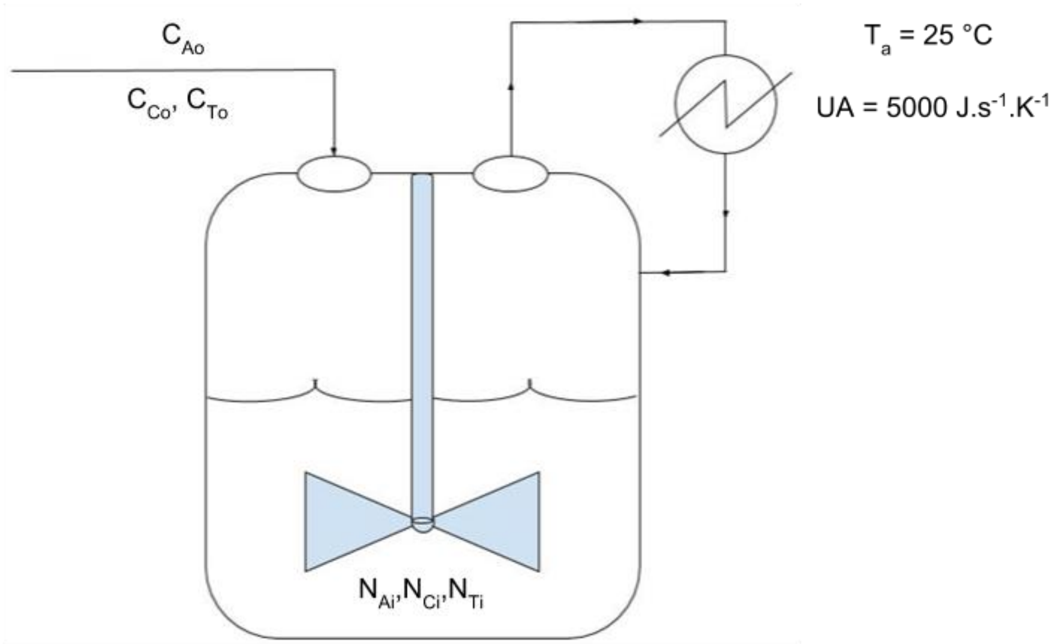

Figure W13-1: Semibatch reactor of Synthron explosion

Before reading further, view the Chemical Safety Board (CSB) video (time 2:00-7:00) on the Synthron explosion. The incident report can also be viewed for more detail. The links are as follows:

CSB video: (https://www.youtube.com/watch?v=sRuz9bzBrtY)

The incident report can also be viewed for more detail.

Incident report: (https://www.csb.gov/file.aspx?DocumentId=5619)

The reaction takes place in two distinct stages. First, the reactor is initially loaded with n-butyl acrylate, as well as cyclohexane and toluene to be used as solvents. The mixture is heated to its normal boiling point (82°C) and activated by quickly adding small amounts of benzoyl peroxide initiator. Second, as the initial n-butyl acrylate reacts, the rest of the n-butyl acrylate, along with benzoyl peroxide in toluene and cyclohexane is slowly added to the reactor in semi-batch mode.

The order which prompted the accident was 12% more than a standard batch size, and in order to save time and efforts, the entire thing was produced in a single batch instead of two smaller batches. The conditions for the standard and modified recipes are given in Table W13-1.

Table W13-1: Initial conditions of Modarez MFP-BH reaction

Components	Standard Recipe		Modified Recipe	
	Initial Charge $[kmol]$	Feed Concentration $[kmol \cdot m^{-3}]$	Initial Charge $[kmol]$	Feed Concentration $[kmol \cdot m^{-3}]$
n-butyl acrylate	1.55	2.22	5.67	3.99
Cyclohexane	2.64	3.52	7.76	1.94
Toluene	2.20	2.92	7.09	2.09
Feed Rate	$V_o = 0.73\, m^3;\ v_o = \ 1.5 \cdot 10^{-4} \frac{m^3}{s}$		$V_o = 2.38\, m^3; v_o = 6 \cdot 10^{-5} \frac{m^3}{s}$	

(a) Plot the reactor temperature, concentrations of reactant (n-butyl acrylate) and product (Modarez MFP-BH), and heat generated on separate graphs as a function of time

Additional information:

The cooling capacity of the condenser is 30 $\frac{kg}{hr}$. The coolant in the condenser is water at 25°C with a very high flow rate. The rate law is second order for n-butyl acrylate.

With $k(300K) = 0.0358\, L \cdot mol^{-1} \cdot s^{-1}$, and $\frac{E_A}{R} = 28991.6\, K$

$\Delta H^{\circ}_{Rx} = \ -64{,}512\, kJ/kmol$

$UA = 5000\, J \cdot s^{-1} \cdot K^{-1}$

Physical Properties				
Component	Molecular Weight $[kg \cdot kmol^{-1}]$	Density $[kg \cdot m^{-3}]$	Sp. Heat $[kJ \cdot kmol^{-1} \cdot K^{-1}]$	Heat of Vaporization $[kJ \cdot kg^{-1}]$
n-butyl acrylate	128	870	245.75	278
Cyclohexane	84	750	161.30	360
Toluene	92	840	165.60	360
Poly- butyl acrylate			231.00	292

Solution

1. Mole Balances: (See Chapter 6)

N-butyl acrylate (Referred to as A)-

$$F_{Ao} - 0 + r_A \cdot V = \frac{dN_A}{dt}$$

With $F_{Ao} = C_{Ao} \cdot v_o$; $v_o = \frac{dV}{dt}$; $N_A = C_A \cdot V$

Which combines and simplifies to:

$$\frac{dC_A}{dt} = \frac{v_o}{V} \cdot (C_{Ao} - C_A) + r_A; \qquad C_A(0) = \frac{N_{Ai}}{V_o}$$

Cyclohexane (Referred to as C)-

$$\frac{dN_C}{dt} = C_{Co} \cdot v_o; N_C(0) = N_{Ci}$$

Toluene (Referred to as T)-

$$\frac{dN_T}{dt} = C_{To} \cdot v_o; N_T(0) = N_{Ti}$$

Modarez MFP-BH (Referred to as An)-

$$\frac{dN_{An}}{dt} = -r_A \cdot V$$

With $N_{An} = C_{An} \cdot V$;

Gives the following simplification of the left side of the equation:

$$\frac{dN_{An}}{dt} = \frac{d(C_{An} \cdot V)}{dt} = V \cdot \frac{dC_{An}}{dt} + C_{An} \cdot \frac{dV}{dt}$$

Which simplifies as follows:

$$\frac{dC_{An}}{dt} = \left(-C_{An} \cdot \frac{v_o}{V}\right) - r_A; \qquad C_{An}(0) = 0$$

2. Rate Law:

$$-r_A = kC_A^2,$$

3. Stoichiometry:

Since the differential equation for n-butyl acrylate is in terms of concentration, the initial condition also must be concentration:

$$C_{Ai} = \frac{N_{Ai}}{V_o}$$

4. Energy Balance:

The basic form of the energy balance relating temperature and time is as follows:

$$\frac{dT}{dt} = \frac{\dot{Q}_{gs} - \dot{Q}_{rs}}{\sum N_i \cdot C_{pi}}$$

$$\sum N_i \cdot C_{pi} = N_A \cdot C_{pA} + N_C \cdot C_{pC} + N_T \cdot C_{pT} + N_{An} \cdot C_{pAn}$$

Heat generation comes from the heat of reaction:

$$\dot{Q}_{gs} = (r_A \cdot V)(\Delta H_{Rx})$$

Heat removal comes from the flow of inerts in the system, the heat exchange fluid, and the vaporization of reaction materials if the temperature in the reactor exceeds its normal boiling point.

$$Heat\ Removed\text{: } \dot{Q}_{rs} = \dot{Q}_{rs_1} + \dot{Q}_{rs_2} + \dot{Q}_{rs_3}$$

$$Flow\text{: } \dot{Q}_{rs_1} = \sum F_{io} \cdot C_{pi}(T - T_{io})$$

$$\dot{Q}_{rs_1} = (F_{Ao}C_{P_A} + F_{Co}C_{P_C} + F_{To}C_{P_T}) \cdot (T - T_o)$$

$$Heat\ Exchanger\text{: } \dot{Q}_{rs_2} = UA \cdot [T - T_a]$$

$$Vaporization\text{: } \dot{Q}_{rs_3} = \sum \dot{m}_i \cdot \Delta H_{vi}$$

$$\dot{Q}_{rs_3} = \dot{m}_{V_A} \cdot \Delta H_{v_A} + \dot{m}_{V_C} \cdot \Delta H_{v_C} + \dot{m}_{v_T} \cdot \Delta H_{v_T}$$

$$\dot{Q}_{rs_3} = \dot{m}_v \cdot (\Delta H_{v_A} +\cdot \Delta H_{v_C} +\cdot \Delta H_{v_T})$$

Because as the system forms a constant boiling mixture, the masses and evaporation rates of all material in the mixture are approximately equal.

5. Combine/Evaluate:

The standard recipe and modified recipe can be solved in the same manner in preparation for solving of the differential equations and plotting.

Standard Recipe-

$$C_{Ai} = \frac{1.55\ kmol}{0.73\ m^3} = 2.12 \frac{kmol}{m^3}$$

$$\boldsymbol{F_{Ao}} = 2.22 \frac{kmol}{m^3} \cdot 1.5 \cdot 10^{-4} \frac{m^3}{s} = \mathbf{3.33 \cdot 10^{-4}} \boldsymbol{\frac{kmol}{s}}$$

$$\boldsymbol{F_{Co}} = 3.52 \frac{kmol}{m^3} \cdot 1.5 \cdot 10^{-4} \frac{m^3}{s} = \mathbf{5.28 \cdot 10^{-4}} \boldsymbol{\frac{kmol}{s}}$$

$$\boldsymbol{F_{To}} = 2.92 \frac{kmol}{m^3} \cdot 1.5 \cdot 10^{-4} \frac{m^3}{s} = \mathbf{4.38 \cdot 10^{-4}} \boldsymbol{\frac{kmol}{s}}$$

$$F_{Ao}C_{P_A} = 3.33 \cdot 10^{-4}\,\frac{kmol}{s} \cdot 245.75\,\frac{kJ}{kmol \cdot K} = 81.835 \cdot 10^{-3}\,\frac{kJ}{s \cdot K}$$

$$F_{Co}C_{P_C} = 5.28 \cdot 10^{-4}\,\frac{kmol}{s} \cdot 161.30\,\frac{kJ}{kmol \cdot K} = 85.166 \cdot 10^{-3}\,\frac{kJ}{s \cdot K}$$

$$F_{To}C_{P_T} = 4.38 \cdot 10^{-4}\,\frac{kmol}{s} \cdot 165.60\,\frac{kJ}{kmol \cdot K} = 72.533 \cdot 10^{-3}\,\frac{kJ}{s \cdot K}$$

$$F_{Ao}C_{P_A} + F_{Ao}C_{P_A} + F_{Ao}C_{P_A} = (81.835 + 85.166 + 72.533) \cdot 10^{-3} = 239.53 \cdot 10^{-3}\,\frac{kJ}{s \cdot K}$$

$$\boldsymbol{\dot{Q}_{rs_1}} = \left(F_{Ao}C_{P_A} + F_{Co}C_{P_C} + F_{To}C_{P_T}\right) \cdot (T - T_o) = \boldsymbol{239.534 \cdot 10^{-3} \cdot (T - T_o)}$$

$$\dot{m_v} = 30\,\frac{kg}{hr} \cdot \frac{1\,hr}{3600\,s} = \frac{1}{120}\,\frac{kg}{s}$$

$$\dot{Q}_{rs_3} = \dot{m_v} \cdot \left(\Delta H_{v_A} +\cdot\, \Delta H_{v_C} +\cdot\, \Delta H_{v_T}\right) = \frac{1}{120}\,\frac{kg}{s} \cdot (278 + 360 + 360)\,\frac{kJ}{kg} = \boldsymbol{8.316\,\frac{kJ}{s}}$$

Modified Recipe-

$$C_{Ai} = \frac{5.67\,kmol}{2.38\,m^3} = 2.38\,\frac{kmol}{m^3}$$

$$\boldsymbol{F_{Ao}} = 3.99\,\frac{kmol}{m^3} \cdot 6 \cdot 10^{-5}\,\frac{m^3}{s} = \boldsymbol{2.394 \cdot 10^{-4}\,\frac{kmol}{s}}$$

$$\boldsymbol{F_{Co}} = 1.94\,\frac{kmol}{m^3} \cdot 6 \cdot 10^{-5}\,\frac{m^3}{s} = \boldsymbol{1.164 \cdot 10^{-4}\,\frac{kmol}{s}}$$

$$\boldsymbol{F_{To}} = 2.09\,\frac{kmol}{m^3} \cdot 6 \cdot 10^{-5}\,\frac{m^3}{s} = \boldsymbol{1.254 \cdot 10^{-4}\,\frac{kmol}{s}}$$

$$F_{Ao}C_{P_A} = 2.394 \cdot 10^{-4}\,\frac{kmol}{s} \cdot 245.75\,\frac{kJ}{kmol \cdot K} = 58.832 \cdot 10^{-3}\,\frac{kJ}{s \cdot K}$$

$$F_{Co}C_{P_C} = 1.164 \cdot 10^{-4}\,\frac{kmol}{s} \cdot 161.30\,\frac{kJ}{kmol \cdot K} = 18.775 \cdot 10^{-3}\,\frac{kJ}{s \cdot K}$$

$$F_{To}C_{P_T} = 1.254 \cdot 10^{-4}\,\frac{kmol}{s} \cdot 165.60\,\frac{kJ}{kmol \cdot K} = 20.766 \cdot 10^{-3}\,\frac{kJ}{s \cdot K}$$

$$F_{Ao}C_{P_A} + F_{Ao}C_{P_A} + F_{Ao}C_{P_A} = (58.832 + 18.775 + 20.766) \cdot 10^{-3} = 98.373 \cdot 10^{-3}\,\frac{kJ}{s \cdot K}$$

$$\boldsymbol{\dot{Q}_{rs_1}} = \left(F_{Ao}C_{P_A} + F_{Co}C_{P_C} + F_{To}C_{P_T}\right) \cdot (T - T_o) = \boldsymbol{98.373 \cdot 10^{-3} \cdot (T - T_o)}$$

$$\dot{m_v} = 30\,\frac{kg}{hr} \cdot \frac{1\,hr}{3600\,s} = \frac{1}{120}\,\frac{kg}{s}$$

$$\dot{Q}_{rs_3} = \dot{m_v} \cdot (\Delta H_{v_A} +\cdot\, \Delta H_{v_C} +\cdot\, \Delta H_{v_T}) = \frac{1}{120}\,\frac{kg}{s} \cdot (278 + 360 + 360)\,\frac{kJ}{kg} = \boldsymbol{8.316\,\frac{kJ}{s}}$$

The Polymath program and solution results in both table and graphical forms are shown below. The graphical output of the Polymath Program is given in terms of temperature, concentrations, and heat generated versus time to provide meaningful comparison between the original and modified recipes.

Calculated Values of DEQ Variables

	Variable	Initial Value	Final Value		Variable	Initial Value	Final Value
1	Cas	2.12	0.0862826	29	Ca	2.38	0.0475881
2	Cans	0	2.071853	30	Can	0	2.445615
3	Caos	2.22	2.22	31	Cao	3.99	3.99
4	Ccos	3.52	3.52	32	Cco	1.94	1.94
5	Ctos	2.92	2.92	33	Ctp	2.09	2.09
6	Faos	0.000333	0.000333	34	Fao	0.0002394	0.0002394
7	Fcos	0.000528	0.000528	35	Fco	0.0001164	0.0001164
8	Ftos	0.000438	0.000438	36	Fto	0.0001254	0.0001254
9	ks	0.216738	0.0371627	37	k	0.216738	0.0390291
10	Nas	1.5476	0.1018134	38	Na	5.6644	0.1218254
11	Nans	0	2.44787	39	Nan	0	6.260775
12	Ncs	2.64	4.224	40	Nc	7.76	8.1092
13	Ncps	1170.475	1853.016	41	Ncp	3817.818	4020.594
14	Nts	2.2	3.514	42	Nt	7.09	7.4662
15	Qgss	4.59E+04	21.06084	43	Qgs	1.89E+05	14.59706
16	Qrs1s	10.77903	-2.15985	44	Qrs1	4.426835	-0.7612969
17	Qrs2s	285	14.91558	45	Qrs2	285	21.30603
18	Qrss	304.079	21.05573	46	Qrs	297.7268	28.84473
19	ras	-0.9741075	-0.0002767	47	ra	-1.227691	-8.84E-05
20	Ts	355	300.9831	48	T	355	302.2612
21	Vs	0.73	1.18	49	V	2.38	2.56
22	vos	0.00015	0.00015	50	vo	6.00E-05	6.00E-05
23	Vos	0.73	0.73	51	Vo	2.38	2.38
24	Cpa	245.75	245.75				
25	Cpan	231	231				
26	Cpc	161.3	161.3				
27	Cpt	165.6	165.6				
28	t	0	3000				

Differential equations (standard case)

d(Cas)/d(t) = (vos/Vs)*(Caos-Cas) + ras
d(Ncs)/d(t) = Ccos*vos
d(Nts)/d(t) = Ctos*vos
d(Cans)/d(t) = -ras - (Cans*(vos/Vs))
d(Ts)/d(t) = (Qgss-Qrss)/NCps

Explicit equations (standard case)

Caos = 2.22
Ccos = 3.52
Ctos = 2.92
Vos = 0.73
vos = 1.5*10^-4
Vs = Vos + (vos*t)
Cpa = 245.75
Cpc = 161.3
Cpt = 165.60
Cpan = 231
Nas= Cas*Vs
Nans = Cans*Vs
Faos = Caos*vos
Fcos = Ccos*vos
Ftos= Ctos*vos
ks = 4.01*10^3**exp*(-29000/(8.314*Ts))
ras = -ks*(Cas^2)
Qgss = -ras*Vs*64512
Qrs1s = ((Faos*Cpa)+(Fcos*Cpc)+(Ftos*Cpt))*(Ts-310)
Qrs2s = 5*(Ts-298)
Qrss= Qrs1s+Qrs2s+8.3
NCps = (Nas*Cpa)+(Ncs*Cpc)+(Nts*Cpt)+(Nans*Cpan)

Differential equations (modified case)

d(Ca)/d(t) = (vo/V)*(Cao-Ca) + ra
d(Nc)/d(t) = Cco*vo
d(Nt)/d(t) = Cto*vo
d(Can)/d(t) = -ra - (Can*(vo/V))
d(T)/d(t) = (Qgs-Qrs)/NCp

Explicit equations (modified case)
Cao = 3.99
Cco = 1.94
Cto = 2.09
Vo = 2.38
vo = 6*10^-5
V = Vo + (vo*t)
Na= Ca*V
Nan = Can*V
Fao = Cao*vo
Fco = Cco*vo
Fto= Cto*vo
k = 4.01*10^3**exp*(-29000/(8.314*T))
ra = -k*(Ca^2)
Qgs = -ra*V*64512
Qrs1 = ((Fao*Cpa)+(Fco*Cpc)+(Fto*Cpt))*(T-310)
Qrs2 = 5*(T-298)
Qrs= Qrs1+Qrs2+8.3
NCp = (Na*Cpa)+(Nc*Cpc)+(Nt*Cpt)+(Nan*Cpan)

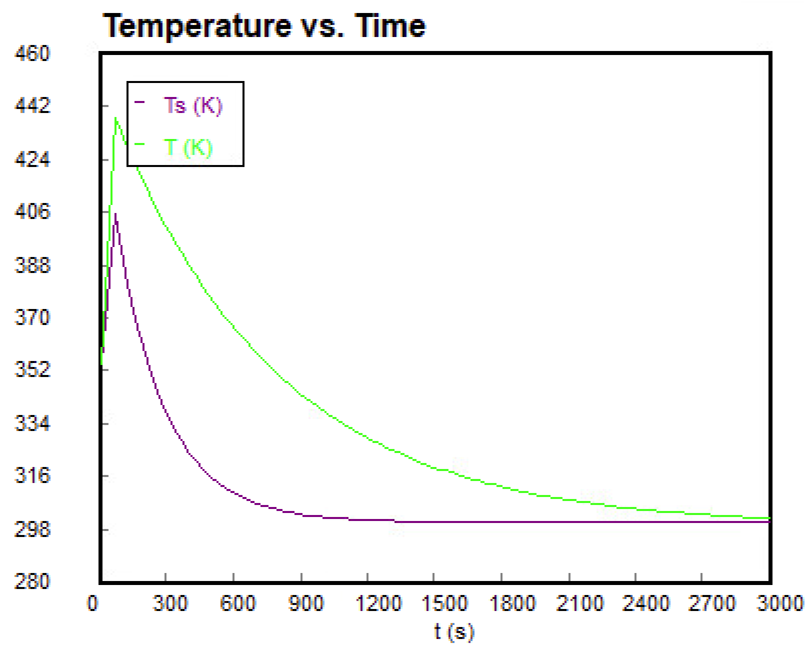

Figure W13-2: Temperature vs. Time Polymath Plot

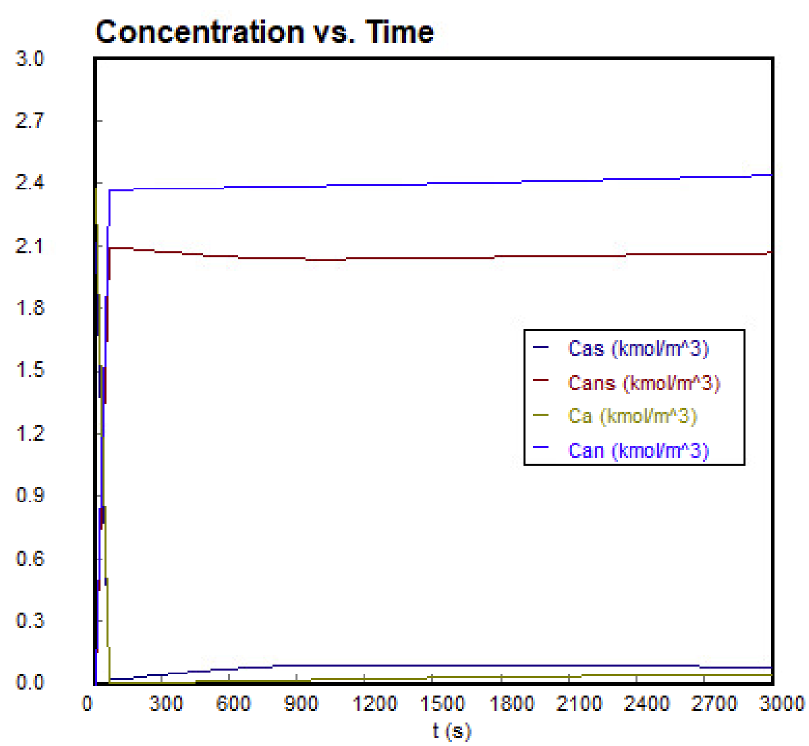

Figure W13-3: Concentration vs. Time Polymath Plot

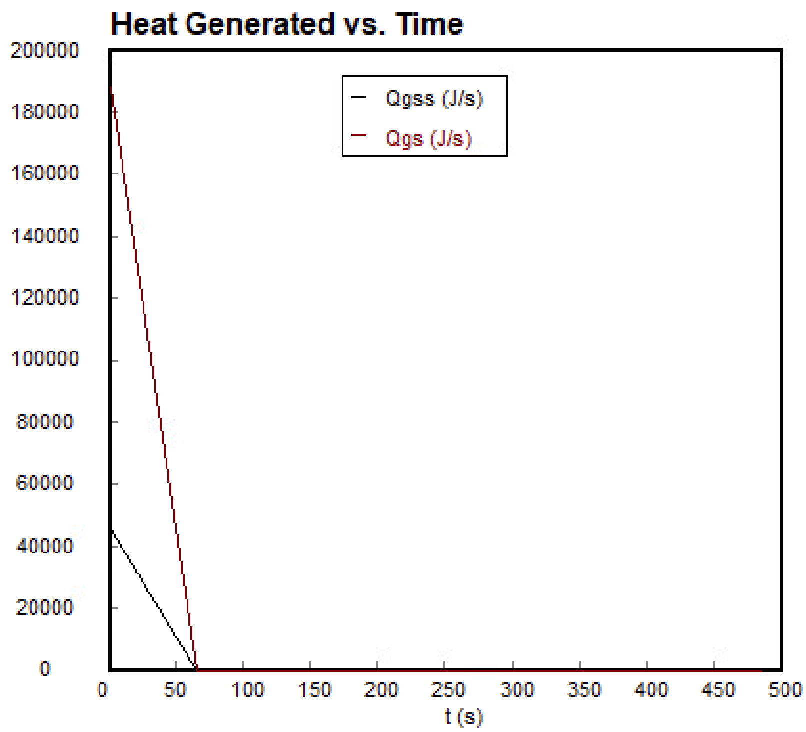

Figure W13-4: Heat Generated vs. Time Plot

Analysis:

It is immediately evident from looking at the three figures that the modified reaction is going to be a problem immediately from time zero. The heat generated at time=0 for the modified recipe is approximately 5 times greater than the standard recipe from Synthron. The rate of cooling fluid in the reaction was designed such that the heat removed was sufficient to account for the exothermic nature of the reaction. However, if the cooling fluid only has capacity to remove the amount of heat generated from the original recipe, that still leaves 143,000 J of energy unaccounted for. This large amount of heat generated in the system causes the large temperature spike, pushing the system to temperatures of ~440K instead of the standard ~405K. The large amount of heat generated at time t=0 is also indicative of a higher initial rate of reaction, which can be seen in the second graph, which shows the amount of product produced is immediately higher in the modified case. In reality, the large amount of heat that is unable to be removed from the system begins to increase the pressure of the reactor as well as the temperature. The increase in pressure is what eventually causes the vapor leak as well as the explosion, but the pressure is not modeled in this module due to the complicated differential equation it brings into the system. Overall, the large amount of reactants initially present in the system put the reaction in a dangerous position immediately. This module shows the importance of taking note of what effect changing reaction conditions can have on a system. The workers at Synthron did not take into account the temperature spike that would occur from the large amount of initial reactants, and this oversight proved fatal.