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Runaway Reactions and Vapor Cloud Explosions: the Synthron Case Study

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Thermal runaway in chemical batch and semibatch reactors is one of the major plagues in fine chemical, pharmaceutical and plastic industries. Quite often the root cause of such events is a poor knowledge of the process kinetics and thermodynamics. For this reason, accidents continue to occur with a high frequency in both European and American countries.

The present work is focused on the accident occurred in 2006 at Synthron Inc. (Morganton, NC), an American company that manufactured a great variety of powder coatings and paint additives. The accident has been originated by a runaway reaction and subsequent vapor cloud explosion (that killed one worker and injured 14 others) due to a wrong scaling-up of the original process recipe. Particularly, the standard synthesis was carried out in a 1,500 gallon semibatch reactor by polymerizing liquid acrylic monomers in a high flammable solvent blend. On the day of the accident, in order to produce slightly more of the desired product, plant managers decided to scale-up the process recipe in a single larger batch. In order to perform the synthesis in the same time of the standard recipe, they also decided to load almost all of the additional monomer required into the initial reactor charge: that is, using a quasi-batch operating mode.

Unfortunately, adding all the monomer in one shot, more than doubled the rate of energy release in the reactor, exceeding the cooling capacity of the equipped condenser and causing a runaway reaction. The reactor pressure increased rapidly. Solvent vapors, vented from the reactor's rupture disc, formed a flammable cloud inside the building, found an ignition source and, finally, resulted in a violent explosion.

This work presents a detailed reconstruction of the dynamics of the accident occurred at Synthron Inc. using all data collected by the U.S. Chemical Safety Board (CSB) and implementing a detailed mathematical model capable of describing monomer conversion, temperature and pressure evolution inside the reactor together with the condenser efficiency. Particularly, all constitutive equations of material and energy balance, dosing policies and mixing rules have been considered. Results arising from simulations have been found to be in good agreement with both CSB collected data and successive reconstructions.

1. Introduction

Runaway reactions can be considered one of the major plagues affecting safety in fine chemical, pharmaceutical and plastic industries (Jiang et al., 2011; Copelli et al., 2012).

Particularly, such an unwanted phenomenon consists in a loss of the reactor temperature control during the synthesis that occurs whenever the rate of heat evolution is higher than the rate at which the heat can be readily removed by an installed cooling equipment (cooling jacket or coil, condenser, etc..).

Often, such critical reactions are carried out in semibatch reactors (SBRs) where one or more reactants are dosed on an already loaded mixture in order to control the rate of heat generation by the feeding rate (Maestri et al., 2009; Copelli et al., 2011). However, if the process is operated under high accumulation conditions, the desired reaction thermal control may be lost and the reactor temperature may increase up to values at which secondary undesired reactions or decompositions of the reacting mixture are triggered

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(Maschio et al., 2010). Such reactions, apart from a reduction of the selectivity with respect to the desired product, may lead to a real system thermal loss of control because they are usually much more fast and exothermic than the desired reaction. Moreover, if a decomposition event is triggered because of the system thermal loss of control, the consequent release of incoercible gases may pressurize the reactor leading to its venting through the installed emergency pressure relief system and, eventually, to its physical explosion.

On the contrary, if the reacting mass cannot undergo a decomposition event, the heat released during the loss of control of the desired reaction may trigger an unwanted mixture boiling that, producing high quantities of vapors in short times, may rapidly pressurize the reactor and lead to its venting (as in the case of the triggering of a decomposition reaction). Moreover, if the vapors vented from the reactor are hazardous (e.g., flammable or toxic) and the venting system is not connected to a suitable abatement unit, the secondary effects (such as fires, vapor cloud explosions or toxic clouds) can affect a large region around the reactor.

Terrible examples of such scenarios are Seveso (1976) and Bhopal (1984) accidents. Minor and recent examples are: 1) the T2 laboratories accident in Jacksonville, Florida (2007), where 4 workers died and 32 people were injured; 2) the Bayer CropScience LP, West Virginia (2008), where 2 workers died and 8 people were injured and 3) the Synthron Inc., Morganton, NC (2006), where one worker died and 14 others were injured.

Independently of the magnitude of the runaway phenomena, quite often the root cause of such accidents is a poor knowledge of the process kinetics and thermodynamics. Particularly, there is a frequent misunderstanding in between the concepts of heat (thermodynamics) and power (kinetics) released by an exothermic reaction. In fact, the real danger of a potentially runaway process is not only how much heat can be released during the synthesis (that is, the reaction enthalpy, J/kmol) but also at which rate such a heat is released (that is, the reaction enthalpy multiplied by the reaction rate, W/kmol). A slow but highly exothermic reaction is generally much safer than a very fast even if less exothermic one.

The present work has been focused on the accident occurred at Synthron Inc. (Morganton, NC) in 2006. The accident, originated by a runaway chemical reaction, killed one worker and injured 14 others (two seriously). Moreover, the vapor cloud explosion generated by the venting of high flammable solvent vapors into the plant destroyed the facility and damaged some structures in the nearby community.

Particularly, a detailed reconstruction of the dynamics of the accident occurred at Synthron Inc. has been performed using all data collected by the U.S. Chemical Safety Board (CSB) and implementing a detailed mathematical model capable of describing monomer conversion, temperature and pressure evolution inside the reactor together with temperatures and vapor flow rate inside the condenser at the top of the reactor. Moreover, all constitutive equations of material and energy balance, dosing policies (semibatch, during normal conditions, and quasi-batch, during the accident) and mixing rules have been considered. Results arising from simulations have been found to be in good agreement with both CSB collected data and successive reconstructions.

2. Accident Description

Synthron Inc. is a company that manufactured a great variety of powder coatings and paint additives by polymerizing acrylic monomers of different kinds.

On January 31, 2006, a runaway reaction occurred at Synthron while employees were making the product Modarez MFP-BH (CSB, 2007). This polymerization reaction has been performed for years in a 1,500 gallon Pfaudler reactor (M-1) using a blend of toluene and cyclohexane as solvents, n-butyl acrylate as monomer and benzoyl peroxide as initiator. Particularly, the reactor M-1 was equipped with the following devices: an external jacket, dedicated to both heating and cooling, an anchor stirrer and a reflux condenser, located at the top of the reactor. A standard plant recipe scheduled the following operational steps: 1) loading the reactor with a blend of toluene, cyclohexane and n-butyl acrylate; 2) heating the reactor by injecting vapor into the jacket until the desired temperature (usually the mixture normal boiling point) was reached; 3) activating the reaction triggering sequence, that is dosing at high feeding rate a small amount of initiator solution (constituted by toluene, cyclohexane and benzoyl peroxide); 4) waiting enough time to permit the reaction triggering and the exothermic effect depletion; 5) starting to dose slowly (approximately, 4 h) the remaining quantities of monomer and initiator solution. Table 1 reports the standard recipe used by Synthron Inc. until the day of the accident.

Just some time before January 31, 2006, the company had received an order for slightly more of an additive than the normal size recipe would have produced (CSB, 2007). Plant managers decided to scale-up the recipe to produce the required larger amount of polymer by adding almost all of the additional monomer needed into the initial charge. It is worth to notice that, in the original recipe, the process was carried out loading only a little quantity of the required monomer (about 25 % w/w of the total amount) at the beginning of the synthesis step, while the remaining amount was dosed successively (semibatch operating mode).

Table 1: Standard and modified recipe for the synthesis of Modarez MFP-BH

	Standard recipe			Modified recipe		
	Initial charge	Dosing during triggering step	Final Dosing	Initial charge	Dosing during triggering step	Final Dosing
	kg	kg	kg	Kg	Kg	kg
n-butyl acrylate	199	0	596	726	0	426
Benzoyl peroxide	0	1.15	3.50	0	4.20	2.50
Toluene	191	11.50	563	610	42	160
Cyclohexane	210	11.50	620	610	42	136

On the day of the accident, according to the employer's records, there were 1,220 kg of the solvent blend and 726 kg of n-butyl acrylate (about 63% w/w of the total amount) in the reactor M-1, ready to be processed. The senior operator responsible for the synthesis started to add steam to the external jacket to heat the reactor to the specified reaction temperature (about 82-85 °C); then, he shut off the steam. The further step scheduled on the recipe was to trigger the reacting mixture by adding the initiator solution. Such a blend was contained in two 55-gallon drums and one 330-gallon IBC tote that were positioned in front of the reactor. Immediately after the shut off of the steam, the operator started to dose quickly the initiator solution (triggering phase). The contents of one of the drums and a portion of a second drum had been transferred to the M-1 reactor, when the operator walked away from the reactor, intending to turn a valve on the M-5 reactor (that contained the remaining monomer to be fed during the “dosing phase”) to begin a nitrogen purge and move the contents of M-5 to M-1. While walking down a stair to perform this task, he heard a loud hissing and observed that some vapors were exiting from the reactor manway. The irritating vapor forced him out of the building together with other three employees. Joined by the plant superintendent and the plant manager, the employees gathered outside an upper level doorway. Then, the senior operator re-entered the building wearing a respirator in order to start the emergency cooling water flow to the reactor jacket. But this emergency procedure resulted useless because the building exploded less than 30 seconds after he exited. Twelve employees and two bystanders sustained various injuries. Five of the employees were hospitalized with various injuries, and one died later of burns.

3. Mathematical Model

In the following it will be presented the mathematical model used to simulate the Synthron process under both normal and modified operating conditions.

3.1 Kinetic Scheme

The reaction to be carried out is a free radical solution homopolymerization of butyl acrylate in a blend of toluene and cyclohexane. This polymerization is thermally initiated by benzoyl peroxide and it is performed in a semibatch reactor under reflux operating conditions (that is, the heat of reaction is removed mainly by using a condenser located at the top of the reactor). The kinetic scheme that has been adopted in this work involves the following main reactions (Copelli et al., 2011): initiation (i), propagation of secondary (or terminal or S) radicals (ps), backbiting (bb), propagation of tertiary (or midchain or T) radicals (pt) and termination by combination (tss, ttt and tst; according to the fact that two radical species have been hypothesized to exist).

3.2 Material Balance Equations

In order to completely characterize the kinetic scheme previously presented, the following material balance equations on:
initiator:

$$dn_I/dt = F_I - r_i \cdot V \tag{1}$$

radicals of type S and T:

$$dn_S/dt = 2 \cdot r_i \cdot V + r_{pt} \cdot V - r_{bb} \cdot V - 2 \cdot r_{tss} \cdot V - r_{tst} \cdot V \tag{2}$$

$$dn_T/dt = -r_{pt} \cdot V + r_{bb} \cdot V - 2 \cdot r_{ttt} \cdot V - r_{tst} \cdot V \tag{3}$$

and monomer:

$$dn_M/dt = -\left(r_{ps} + r_{pt}\right) \cdot V \tag{4}$$

are required. For the equations (1) to (4): n_I is the initiator number of moles, kmol; F_I is the initiator molar flow rate, kmol/s; r_i is the rate of initiator thermal decomposition, 1/s; $n_{S/T}$ is the number of moles of radicals of type S or T, kmol; $r_{ps/pt}$ is the rate of propagation of secondary (or tertiary) radicals, kmol/(m^3 s); r_{bb} is the rate of the backbiting reaction, kmol/(m^3 s); $r_{tss/ttt/tst}$ is the rate of the termination by combination reaction (SS, TT or ST), kmol/(m^3 s); n_M is the monomer number of moles, kmol; and V is the liquid volume, m^3.

3.3 Global Material Balance

In order to evaluate the overall liquid volume, it has been hypothesized that: 1) simple additivity of volumes (ideal liquid solution) occurs; 2) densities are quite constant with temperature; 3) there is a volume contraction whenever monomer converts to polymer; 4) solvent vapors are evolved from the reacting mixture during the synthesis and, successively, condensed. Moreover, since the heat exchanger at the top of the reactor may be not able to condensate all the evaporated solvent (partial reflux), only a fraction x of the total evaporating flowrate come back to the liquid phase of the reactor.

The resulting global material balance on the liquid phase in the reactor is:

$$\frac{d\rho}{dt} \cdot V + \rho \cdot \frac{dV}{dt} = \frac{dm_{dos}}{dt} - (1-x) \cdot \frac{dm_{evap}}{dt} \tag{5}$$

The density derivative with respect to time can be calculated by the following mixing rule:

$$\rho = m/V = m_0 + m_{dos} - (1-x) \cdot m_{evap} \Bigg/ V_0 + \frac{m_{dos}}{\rho_{dos}} \cdot (1 - \alpha \cdot \zeta_M) \tag{6}$$

where ρ is the average liquid density, kg/m^3; m_{dos} is the mass dosed until time t, kg; m_{evap} is the mass evaporated until time t, kg; m_0 is the mass initially loaded into the reactor, kg; V_0 is the initial liquid volume, m^3; α is the volume contraction factor, -; ζ_M is the monomer conversion, -; and subscript dos refers to the dosing streams.

3.4 Rate of evaporation

The rate of evaporation of the solvent may be calculated through the following approximate relation:

$$dm_{evap}/dt = k_p \cdot PM_{solv} \cdot \left[P°_{solv}(T) - P \cdot y_{solv}\right] \cdot S_{evap} + \left(r_{ps} + r_{pt}\right) \cdot V \cdot d\zeta_M/dt \cdot \Delta h_{rxn}/\Delta h_{evap} \tag{7}$$

where: k_p is the material transfer coefficient referred to the partial pressures; PM_{solv} is the average molecular weight of the vapors, kg/kmol; $P°_{solv}(T)$ is the vapor pressure of the solvent, Pa; P is the absolute pressure inside the reactor, Pa; y_{solv} is the molar fraction of solvent into the top of the reactor, -; S_{evap} is the free liquid surface, m^2; Δh_{rxn} is the reaction enthalpy, J/kmol; and Δh_{evap} is the vaporization heat, J/kmol. This equation takes into account the two main contributions to the rate of evaporation, namely: mass transfer due to material gradients in the vapor phase, and evaporation due to the heat provided to the mass by the heat of reaction.

3.5 Condenser Efficiency and Energy Balance

The reactor is equipped with a reflux condenser. In order to better analyze the operation of such an equipment the ε-NTU method, which is a tool for the analysis of a generic heat exchanger when the temperatures of the input and output fluids (in this case, water and solvent) are known (or derivable from an energy balance), has been used. This method is based on the calculation of the maximum thermal power, W_{max}, that can be removed from the heat exchanger. Such a power is obtained by using the lowest thermal capacity between those of the fluids exchanging heat and the maximum temperature gradient in between the fluids themselves (i.e., inlet temperature of the “hot” fluid and inlet temperature of the "cold" fluid). It results:

$$W_{\max} = c_{p,vap} \cdot \left(T - T_{w,IN}\right) \cdot dm_{evap}/dt \tag{8}$$

where $c_{p,vap}$ is the specific heat of the vapors, J/(kg K); T is the temperature, K; and $T_{w,IN}$ is the temperature of the cooling water that enters the condenser, K.

The thermal power actually exchanged between the fluids in the condenser, W, will be given by:

$$W = \varepsilon \cdot W_{\max} = c_{p,w} \cdot \left(T_{w,OUT} - T_{w,IN}\right) \cdot dm_w / dt \tag{9}$$

where $c_{p,w}$ is the specific heat of the liquid water inside the heat exchanger, J/(kg K); $T_{w,OUT}$ is the temperature of the cooling water that exits the condenser, K, and:

$$\varepsilon = 1 - \exp(-NTU) \tag{10}$$

is the condenser efficiency, -, which is a function of the number of transfer unit (NTU), -. Under conditions of partial reflux, it is verified that:

$$[1 - \exp(-NTU)] \cdot W_{\max} = \Delta h_{evap} \cdot x \cdot dm_{evap} / dt \tag{11}$$

from which it is possible to calculate the fraction x of vapors that are effectively condensed and sent back to the liquid phase of the reactor.

Finally, it is necessary to write an energy balance equation on the liquid phase of the reactor in order to determine the temperature of the liquid phase (assumed equal to that of the vapor phase), T:

$$\begin{aligned} \frac{d(m \cdot h)}{dt} &= \frac{dm_{dos}}{dt} \cdot c_{p,dos} \cdot \left(T_{dos} - T_{rif}\right) + V \cdot \left(r_{ps} + r_{ps}\right) \cdot \left(-\Delta h_{rxn}\right) - UA \cdot \left(T - T_{cool}\right) - UA_{ext} \cdot \left(T - T_{amb}\right) \\ &\quad - \frac{dm_{evap}}{dt} \cdot \left[\Delta h_{evap}\left(T_{rif}\right) + c_{p,vap} \cdot \left(T - T_{rif}\right)\right] + x \cdot \frac{dm_{evap}}{dt} \cdot \hat{c}_{p,liq} \cdot \left(T - T_{rif}\right) \end{aligned} \tag{12}$$

where UA and UA_{ext} are the global heat transfer coefficients for the jacket and the environment, W/K, respectively; subscript $cool$ refers to the coolant (or jacket); ref refers to the reference temperature (which has been assumed equal to 300 K); amb refers to the ambient temperature; and subscripts vap and liq refer to the vapors and the liquid phase inside the reactor, respectively.

3.6 Pressure

The internal pressure (i.e., in the total volume V_{TOT} occupied by vapors within both the reactor and the condenser) can be computed by differentiating the ideal gas law. Since before starting the process the reactor is purged with nitrogen, it results that:

$$\frac{dP}{dt} \cdot \left(V_{TOT} - V\right) - P \cdot \frac{dV}{dt} = R \cdot \left[\frac{T \cdot (1-x)}{PM_{vap}} \cdot \frac{dm_{evap}}{dt} + \left(n_0 + \frac{(1-x) \cdot m_{evap}}{PM_{vap}}\right) \cdot \frac{dT}{dt}\right] \tag{13}$$

where: R is the ideal gas constant, 8.314 J/(mol K) and n_0 is the initial number of moles in the gas phase, kmol.

3.7 Control Equation

Finally, a suitable control equation expressing the dosing policy (in this case, constant feeding rate) complements the system of ordinary differential equations needed to simulate the dynamics of the Synthron process under both normal and upset operating conditions:

$$\begin{cases} \dfrac{dm_{dos}}{dt} = \dfrac{m_{dos,1}}{t_{dos,1}} & 0 \le t < t_{dos,1} \\ \dfrac{dm_{dos}}{dt} = 0 & t_{dos,1} \le t < t_{phase\ 1} \quad and \quad t_{phase\ 1} + t_{dos,2} \le t < t_{phase\ 2} \\ \dfrac{dm_{dos}}{dt} = \dfrac{m_{dos,2}}{t_{dos,2}} & t_{phase\ 1} \le t < t_{phase\ 1} + t_{dos,2} \end{cases} \tag{14}$$

where: $m_{dos,i}$ is the total mass dosed during phase i, kg; and $t_{dos,i}$ is the dosing time in phase i, s.

4. Results

In the following the results of the simulations under both normal and upset operating conditions of the Synthron process are discussed. Particularly, Figure 1 shows a comparison between reactor temperatures in normal and upset conditions, while Figure 2 reports the internal pressure always in normal and upset operating conditions. As it can be noticed, when the standard recipe is used the maximum reactor temperature is reached during the triggering phase and it does not exceed 96 °C. Contextually, at the end of the process, a final pressure of about 2.3 bar is reached. Such a pressure is lower than the threshold value of the M-1 reactor reported by CSB, which was equal to about 2.5 bar; in correspondence of this pressure value the reactor manway starts to leak flammable vapors. However, according to this simulation, even if the maximum pressure is lower than the threshold value the process is carried out under unsafe operating conditions also using the standard recipe; in fact, in these conditions the fraction of vapors condensed is equal to about 0.4, that is, the process is operated under partial condensation. As a matter of fact, being the reactor not equipped with a purge line to safely discharge the vapors not condensed, these conditions lead to the reactor pressurization and cannot be considered fully safe. For what concern the recipe used the day of the accident, a maximum temperature of about 150 °C is expected and the pressure value inside the reactor exceeds the threshold value even during the triggering phase (over 3 bar after 10 min). A confirmation of the reliability of the simulation is the comparison with the total power removed by the condenser that has been found by CSB using reaction calorimetry. Under normal conditions the fouled heat exchanger is able to remove, at most, 310 kW. From the simulation it results that the maximum power to be removed by the condenser during the upset process is about 560 W, which is in agreement with CSB data and successive accident reconstructions.

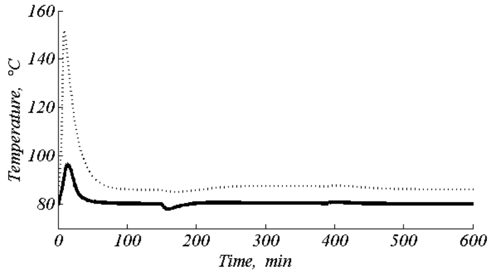

Figure 1: Reactor temperature vs. time under both normal (continuous line) and upset (dotted line) operating conditions

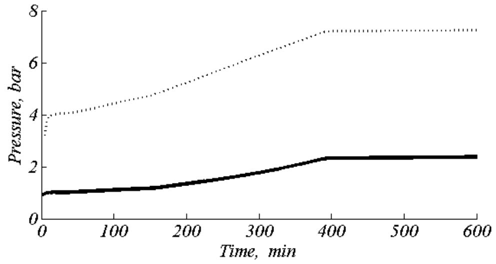

Figure 2: Reactor pressure vs. time under both normal (continuous line) and upset (dotted line) operating conditions

5. Conclusions

In this work a detailed reconstruction of the dynamics of the Synthron Inc. accident has been presented and compared with data collected by the U.S. Chemical Safety Board. Simulations have been carried out by implementing a detailed mathematical model capable of describing the trend of all the process variables in both normal and upset operating conditions. Obtained results have been found to be in agreement with both CSB collected data and successive reconstructions.

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