Safety Promotion of Process Operations in the Chemical Process Industries

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ABSTRACT

This paper discusses how to use the simulation data obtained from the adiabatic reaction calorimeter (ARC) to design the emergency relief systems for chemical reactors and storage vessels to overcome the problem of reactor explosions resulted from excessive pressure and thus the disastrous incidents can be avoided. Here the styrene polymerization reaction is choosen as the reaction system to describe the design of emergency relief system using the ARC data. The simulation results show that the change of the initiator and the monomer concentration will influence the maximun temperature, pressure, and the rate of temperature rise in the reactor. The simulation results also illustrate that in the designing of the emergency relief system, the larger the overpressure is, the smaller the vent diameter will be needed.

INTRODUCTION

Although there are many safety precautions within chemical plants, the problem of reactor explosions due to excessive pressure buildup, which may be caused by reactor failures or operators' errors, will cause major releases of toxic or flammable chemicals and will result in disastrous consequences. In many chemical processes, however, materials need not be reactive or flammable in order to blow up reactors. If one vaporizes liquid in a closed reactor, one must balance the added volume with outflow or with a like amount of condensation elsewhere in the process. Otherwise, the pressure will rise until the reactor failures, and the event will occur in an instant ("explosion in the reactor"). Therefore, providing an adequate pressure relief is necessary for the processes.

A number of investigators (Boyle, 1967; Huff, 1982; Fauske, 1984, 1989; Leung, 1986; Leung and Fisher, 1989) have considered the most realistic situations which are based on the release of a vapor-liquid mixture, with two-phase discharge in the relief system. This paper discusses how to use the theoretical model to calculate required relief area for batch polymerization reactors. The method can be tailored to fit almost any batch polymerization reaction or any other temperature-dependent exothermic chemical reaction.

PROCESS DESCRIPTION

The process model for the free radical solution polymeriza-tion of styrene in the ARC system (Fig. 1), i.e. a batch reactor, involves reaction kinetics, a material balance and an energy balance. The ARC model (Jaisinghani and Ray, 1977) for polystyrene polymerization is

$$\frac{d[I]}{dt} = -kd[I]$$

$$\frac{d[M]}{dt} = -kp[M][P] \tag{1}$$

$$[P] = [\frac{2fkd[I]}{kt}]1/2$$

$$\rho CpV \frac{dTr}{dt} = -\Delta HrVkp[M][P] - hA'(Tr - Tw) \tag{2}$$

with initial conditions

$$t=0,\ [I]=[I]in,\ [M]=[M]in,\ Tr=Trin$$

The physical constants and operating conditions for polystyrene reaction are given in Table 1 (Brooks, 1981; Biesenberger and Sebastian, 1983).

For the polystyrene polymerization, the pressure in the ARC is dependent on the changes of the air partial pressure and the styrene vapor pressure (Huff,1982).

The change of the pressure in the ARC is given in equation 3:

$$Pr = Pair + P0 \qquad (3)$$

where

$$Pair = 0.00282Tr$$

$$\log(P0) = 4.12108 - 1496.44/(Tr - 58.47)$$

At the adiabatic conditions, the temperature (Tra), the pressure (Pra), and the rate of temperature rise (dTra/dt) can be calculated by using the ARC data. The relationship among themselves can be described as follow (Huff,1982):

$$Tra = Tr + (1/aARC)(Tr - Tr1) \qquad (4)$$

$$\log(Pra/Pr)=2140[1/(Tr-273.2+\bar{C}) - 1/(Tra-273.2+\bar{C})] \qquad (5)$$

$$dTra/dt =$$

$$(dTr/dt)(1/aARC)\exp[-(74100/8.319)(1/Tra-1/Tr)] \qquad (6)$$

where

$$aARC = 1/\{1+[(\overline{wC})w(dTw/dt)]/[(\overline{wC})r(dTr/dt)]\}$$

By using the data obtained from equations (4) - (6), we can predict the vent sizing of the polystyrene polymerization reactors under the adiabatic conditions.

HOMOGENEOUS-VESSEL VENTING

The governing equations for relief vent rate requirement can be obtained by considering the macroscopic energy and mass balance on the vessel as shown in Fig. 2. For the bulk of the fluid in the vessel, the energy balance and the mass balance can be described individually as follows:

Energy balance:

$$\frac{d}{dt}(\rho Vu) = Q - W(u1 + \frac{P}{\rho_1}) \qquad (7)$$

Mass balance:

$$\frac{d}{dt}(\rho V) = -W \tag{8}$$

For an ideal gas and an incompressible liquid, the combined material and energy balance is (Leung, 1986; Huff, 1982):

$$mCpf\frac{dTr}{dt} = Q - Whfg(x1 + \frac{vf}{vfg}) \tag{9}$$

In this paper, we only discuss the particular case of zero disengagement of liquid and vapor within the vessel, the so-called uniform-froth or homogeneous-vessel venting case. For this case x1 = x, and v1 = v = V/m; Eq. 9 then takes the form

$$mCp\frac{dTr}{dt} = mq - GA\,\frac{V}{m}\,\frac{hfg}{vfg} \tag{10}$$

By using Eq. 8, Eq. 9, and the turnaround criterion, the result equation for the homogeneous venting rate required to stop the temperature rise with zero disengagement can be obtained:

$$W = GA = \frac{m0q}{[(\frac{V\,hfg}{m0vfg})1/2 + (Cp\ T)1/2]^{2}} \tag{11}$$

where T is simply the "overtemperature (Tm - Ts)". The average heat generation rate q is evaluated from the relationship:

$$q = \frac{1}{2}\,Cp[(\frac{dTr}{dt})s + (\frac{dTr}{dt})m] \tag{12}$$

where (dTr/dt)s and (dTr/dt)m are the self-heat rates at the set temperature and turnaround temperature, respectively. Eq. (11) is a simplified methodology for estimating emergency vent sizes by computations that do not require detailed kinetic data. The key data required for the vent size estimation are the adiabatic self-heat rate, the vapor pressure-temperature relationship and the specific heat of the liquid.

DISCHARGE FLOW MODELS

Leung (1986) has proposed a generalized correlation for HEM (Homogeneous Equilibrium Model) model with the scaling parameter w given entirely in terms of known stagnation properties

$$w = \frac{xvfg}{v} + \frac{CpTrP}{v}\left(\frac{vfg}{hfg}\right)2 \tag{13}$$

In equation form, the generalized correlation gives the following normalized mass flux $G/\sqrt{P/v}$:

For w>4.0 (low-quality region)

$$G/(P/v)^{1/2} = [0.6055 + 0.1356(\ln w) - 0.0131(\ln w)^{2}]/w^{0.5} \tag{14}$$

and for w<4.0 (high-quality region)

$$G/(P/v)^{1/2} = 0.66/w^{0.39} \tag{15}$$

The generalized HEM correlation greatly simplifies the discharge critical flow calculation and is applicable over the entire two-phase region. Furthermore, in the all-liquid inlet condition, to get a good approximation, the correlation may be replaced by

$$G \cong 0.9\,\frac{hfg}{vfg}\left(\frac{1}{CpTr}\right)0.5 \tag{16}$$

In this paper, the generalized HEM correlation (Leung, 1986), Eq. (16), is used to calculate the relief discharge of the styrene polymerization reactor. The process parameters of styrene polymerization reactor is listed in Table 2 (Huff, 1982).

RESULTS

Figures 3 - 5 illustrate the temperature profiles, the pressure profiles, and the rate of temperature rise data for various initiator concentrations. They indicate that the temperature and the pressure in the ARC system will increase when a higher initiator concentration is used. The increase of the temperature and the pressure will affect the sizing of the required vent area for the styrene polymerization reactor. Figure 6 describes that a large vent diameter is needed when the concentration of initiator increases. Because the ARC system is assumed to be a good adiabatic reactor so that the temperature in the ARC system wili not decrease immediately when the styrene polymerization raction comes to the end. Therefore, in Figures 3 and 4, the tail end of the curves stays at a constant value for a while. The same results can be obtained for various styrene monomer concentrations.

Figure 7 is a plot of the rate of temperature rise vs. time. The plot shows the difference of the rate of temperature rise between the observed and the a=1 condition. It is importent to design the required vent area for a reactor to protect the opera-tors and the reactor in safety. The safety of the predicted vent area can be trusted by using the data of a=1 condition (i.e. adiabatic condition). The impact of overpressure on vent size is important in designing an emergency relief system. Figure 8 depicts how the vent diameter varies with overpressure for the styrene polymerization. Here the percent overpressure is defined in terms of gage set pressure as

$$\%\text{overpressure} = \left(\frac{Pm(\text{bar g})}{Ps(\text{bar g})} - 1\right) \times 100 \qquad (17)$$

Figure 12 illustrates an important aspect of homogeneous-vessel venting: a drastic reduction in vent diameter can be obtained with a small overpressure; and at higher overpressure the relative reduction in vent diameter becomes increasingly smaller.

CONCLUSIONS

In this paper, a simple ARC model has been provided to estimate the required vent diameter for styrene polymerization reaction by using the simplified vent sizing equations proposed by Leung in 1986. From the simulation results, we can find that the vent diameter will increase when a higher concentration of the initiator and the styrene monomer is used. Although the vent diameter becomes smaller at higher overpressure, it is not recommended to design the relief system under such high overpressure. Because a slight reduction in area can bring about a drastic increase in peak pressure reached.

REFERENCES

Boyle, W. J. Jr.,"Sizing Relief Area for Polymerization Reactor", Chem. Eng. Prog., 63(8), 61(1967).

Fauske, H. K.,"A Quick Approach to Reactor Vent Sizing", Plant/Operations Progress, 3(3), 145(1984).

Fauske, H. K.,"Emergency Relief System Design for Runaway Chemical Reaction: Extension of the Diers Methodology", Chem. Eng. Res. Des. 67(3), 199(1989).

Huff, J. E., "Emergency Venting Requirements", Plant/Operations Progress, 1(4), 211(1982).

Jaisinghani, R. and W. H. Ray, "On the Dynamic Behavior of a Class Of Homogeneous Continuous Stirred Tank Polymerization Reactors", Chem. Engng Sci., 32, 811(1977).

Leung, J. C., "Simplified Vent Sizing Equations for Emergency Relief Requirements in Reactors and Storage Vessels", AIChE J., 32(10), 1622(1986).

Leung, J. C., and H. G. Fisher, "Two-Phase Flow Venting from Reactor Vessels", J. Loss Prev. Process Ind., 2, 78(April, 1989).

Table 1. Operating conditions and physical constants for polystyrene reaction

Inlet concentrations:

$[I] = 0.005$ mol/l

$[M] = 10.581$ mol/l

Inlet temperature:

$T_r = 352.14$ K

$f = 0.6$

$k_p = 1.06 \times 10^7 \exp(-3557/RT_r)$ (l/mol s)

$k_d = 5.95 \times 10^{13} \exp(-14897/RT_r)$ (s^{-1})(AIBN)

$k_t = 1.25 \times 10^9 \exp(-843/RT_r)$ (l/mol s)

$\rho C_p = 360$ cal/l K

Table 2. Process parameters of styrene polymerization reactor

$V = 13.16\ m^3$ (3,500 gal)

$m_0 = 9{,}500$ kg

$P_s = 4.5$ bar abs.

$P_m = 5.4$ bar abs.(assuming 10% above MAWP)

	4.5 Bar Set	5.4 Bar Peak
v_f, m^3/kg	0.001388	0.001414
v_g, m^3/kg; ideal gas assumed	0.08553	0.07278
C_p, kJ/kg K	2.470	2.514
h_{fg}, kJ/kg	310.6	302.3

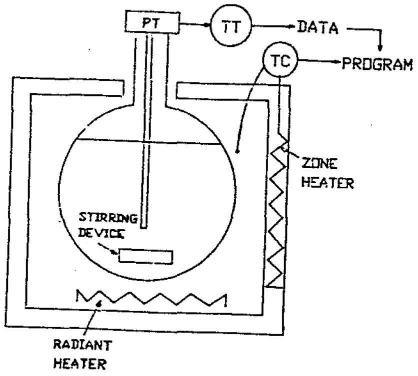

Figure 1. Schematic diagram of the adiabatic reaction calorimeter

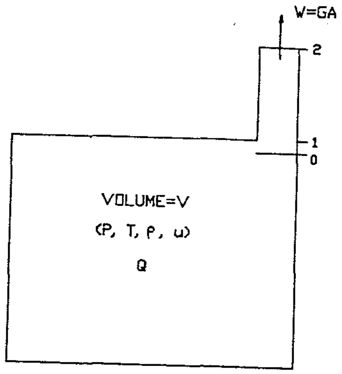

Figure 2. Reference vessel for model development.

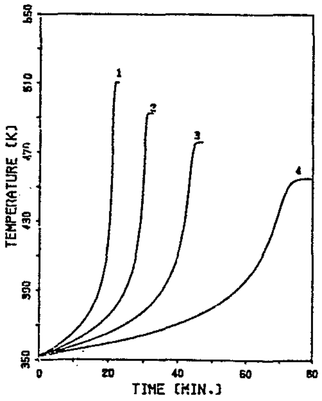

Figure 3. Temperature profiles for various initiator concentrations. ([I]=0.01(1), 0.005(2), 0.0025(3), 0.001(4)).

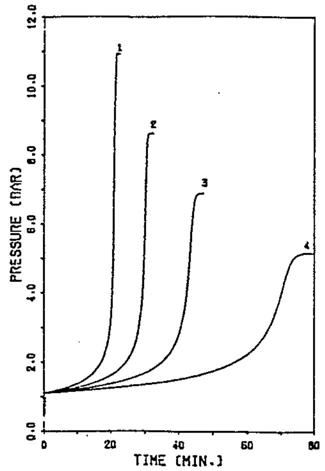

Figure 4. Pressure profiles for various initiator concentrations.
([I]=0.01(1), 0.005(2), 0.0025(3), 0.001(4)).

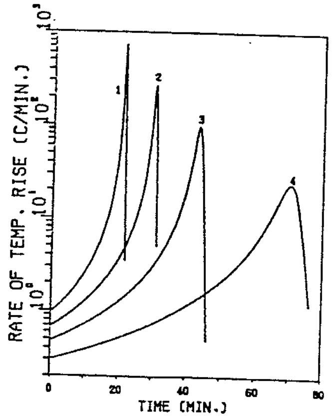

Figure 5. Rate of temperature rise data for various initiator concentrations. ([I]=0.01(1), 0.005(2), 0.0025(3), 0.001(4)).

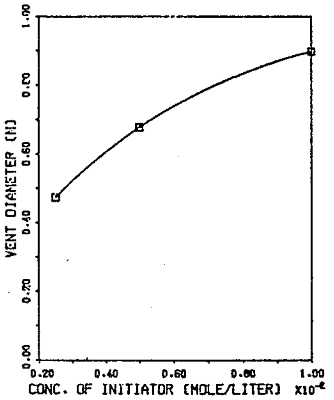

Figure 6. The required vent diameter for various initiator concentrations.

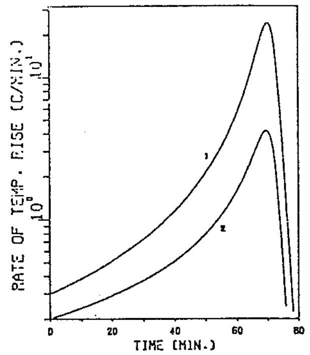

Figure 7. Rate of temperature rise data at various adiabaticity. (a=1(1), raw data(2)).

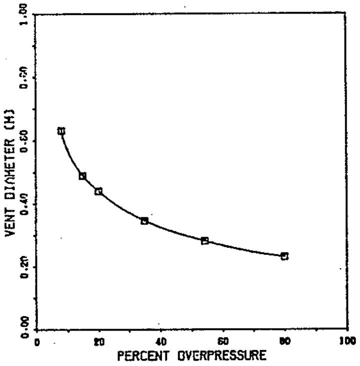

Figure 8. The effect of overpressure on the required vent diameter.