

## **Preventing Phenolic Resin Reactor Accidents:**

## "Easy to Use" Procedure for Checking Adequacy of Emergency Relief Vent Sizes

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Based upon large scale experience Monsanto Company used the following simple vent sizing formula for the phenolic resin reactors (Howard, 1973)

$$D = 0.26 \, (V)^{1/2} \tag{1}$$

where D is the vent diameter in inches and V is the volume of reactants in gallons. It is noted that formula (1) is only applicable for a relief set pressure  $P_s \approx 1.5$  psig (0.103 bar g) and corresponding self heat rate  $\dot{T}_s \approx 6.5^{\circ}\text{C min}^{-1}$ . Formula (1) can be restated as

$$A / V = 9.0 \cdot 10^{-3} \text{ m}^{-1}$$
 (2)

where A  $(m^2)$  is the vent area and V  $(m^3)$  is the volume of reactants. Following Fauske methodology (Fauske, 2006) Eq. 2 can be generalized as follows

A / V = 
$$1.7 \cdot 10^{-3} \frac{\dot{T}_s}{P_s^{1/2}}$$
 (3)

Setting  $\dot{T}_s = 6.5^{\circ}\text{C min}^{-1}$  and  $P_s = 1.5$  psig Eq. 3 results in A/V = 9.0 • 10<sup>-3</sup> m<sup>-1</sup>.

Vent sizing formula (3) is also consistent with dedicated phenolic runaway reaction tests performed by Fauske & Associates with A/V  $\approx 2.8 \cdot 10^{-2}$  (Leung et al., 1998). Considering the most severe tests with  $P_s = 13$  psig and corresponding  $\dot{T}_s = 62^{\circ}$ C, results in

A / V = 
$$1.7 \cdot 10^{-3} \frac{62}{13^{1/2}}$$
  
=  $2.9 \cdot 10^{-2} \text{ m}^{-1}$  (4)

The above observations are consistent with Fauske's generalized vent sizing formula (Fauske, 2006)

$$A/V = \frac{8 \cdot 10^{-4}}{P_s^{1/2}} \frac{\dot{T}_s}{C_D}$$
 (5)

where  $C_D$  is the discharge coefficient determined from  $C_D$  = [1 + 4f L/D]<sup>-0.39</sup> where f = 0.005. Setting  $C_D$  = 0.5,  $P_s$  = 13 psig and  $\dot{T}_s$  = 62°C min<sup>-1</sup> results in A/V = 2.75 • 10<sup>-2</sup> m<sup>-1</sup>, and  $P_s$  = 1.5 psig and  $\dot{T}_s$  = 6.5°C min<sup>-1</sup> results in A/V = 8.5 • 10<sup>-3</sup> m<sup>-1</sup>.

The generalized Monsanto formula (Eq. 3) also clearly explains the 1999 catastrophic vessel failure of a phenol-formaldehyde reactor with A/V =  $6.9 \cdot 10^{-3} \text{ m}^{-1}$  and a relief set pressure  $P_s = 4 \text{ psig}$  (0.276 bar g). The allowable self heat rate  $\dot{T}_s$  for safe relief venting is given by

$$\dot{T}_{s} = \frac{1}{1.7 \cdot 10^{-3}} (A/V) P_{s}^{1/2}$$

$$= \frac{1}{1.7 \cdot 10^{-3}} 6.9 \cdot 10^{-3} \cdot 4^{1/2}$$

$$= 8.1^{\circ} C min^{-1}$$
(6)

which compares to the actual self heat rate of  $\dot{T}_s = 50^{\circ}\text{C min}^{-1}$  at 4 psig obtained by VSP2 calorimetry simulation of the accident.

Using Fauske's generalized formula results in

$$\dot{T}_{s} = \frac{1}{8 \cdot 10^{-4}} (A / V) P_{s}^{1/2} C_{D}$$

$$= \frac{1}{8 \cdot 10^{-4}} 6.9 \cdot 10^{-3} \cdot 4^{1/2} \cdot 0.5$$

$$= 8.6^{\circ} C \min^{-1}$$
(7)

Therefore, formula (5) is recommended as an "easy to use" procedure to check the adequacy of existing reactor relief systems together with appropriate calorimetry testing of  $\underline{\text{credible}}$  worst case scenarios providing the correct values of  $\dot{T}_s$  at relief set pressures  $P_s$  (as low as practical < 5 psig).

## References

Fauske, Hans K., 2006, "Revisiting DIERS' Two-Phase Methodology for Reactive Systems Twenty Years Later," Process Safety Progress, Vol. 25, No. 3, 1998.

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Leung, Joseph C. et al., 1998, "Phenolic Runaway Reaction: Pressure Relief and Containment," Int. Symp. on Runaway Reactions, Pressure Relief Design, and Effluent Handling, March 11-13, 1998, New Orleans, Louisiana, U.S.A.