RUNAWAY PREVENTION IN CUMENE HYDROPEROXIDE STORAGE TANKS

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Abstract

In this work thermal runaway of cumene hydroperoxide (CHP) in a storage tank with constant jacket temperature is considered. The divergence method developed by Strozzi and Zaldivar (1994) based on the concept of parametric sensitivity and a runaway criterion focused on a set of critical parameters identified by Velo et al. (1996) have been applied to our system.

The results obtained from the computer programs derived from the two methods have been compared and discussed. For the case of our interest the boundaries between safe and runaway zones in the parameter space computed according to the divergence method have proved to be too conservative when compared with Velo et al. (1996) results.

Keywords

Runaway, Safe storage, Batch reactor, Thermal decomposition, Cumene hydroperoxide.

Introduction

According to literature on safety many thermal runaways or explosion incidents are caused by the decomposition of organic peroxides due to their thermal instabilities or reactive incompatibilities.

The production of phenol and acetone from cumene (Hercules – BP process) consists of five process operations, i.e. oxidation of cumene to cumene hydroperoxide (CHP), oxidate settling and wash, CHP concentration, cleavage of CHP to phenol and acetone and, in the end, fractionation and purification of cleavage mixture into acetone and phenol.

The transient behavior of the two reaction sections (i.e. oxidation and cleavage) was previously analyzed by means of dynamic simulation in order to point out all those scenarios due to non normal operating conditions that can flow into dangerous situations (Pellegrini et al., 2003).

The present paper focuses on safety regarding the CHP concentration section, that is really the part of the plant where CHP is present in the highest concentration. In particular possible runaways due to overheating in the CHP tanks containing a mixture cumene-CHP with a weight percentage of CHP up to 80% are investigated.

Each tank containing the hydroperoxide can be simulated as a batch reactor with constant surrounding temperature where thermal decomposition can take place.

Dynamic simulation allows also in this case to investigate the time dependent behavior of the process and, possibly, to detect unexpected and unavoidable, potentially dangerous situations. Among the vast amount of parametric sensitivity studies reported in literature both off-line and on-line methods have been analyzed with main regard to the method by Strozzi and Zaldivar (1994) based on divergence computation and the one by Velo et al. (1996).

The Model

The following hypotheses are valid:

- presence of only one exothermic irreversible nth-order reaction with known kinetic;
- well mixing e. g. homogeneous reactor;

- isoperibolic conditions that means constant jacket temperature;
- constant volume as well as physical and transport properties of the reaction mixture;
- no heat accumulation in the reactor wall;
- no change in the effective heat transfer coefficient during the reaction.

The state variables involved are conversion and temperature and the equations necessary to describe the system are mass and energy balances, which, under the previous assumptions, become:

$$\begin{cases} \rho \hat{C}_p V \dfrac{dT}{d\bar{t}} = \left(-\Delta H_R\right) k_0 e^{\left(-\frac{E}{RT}\right)} V \left[C_0\left(1-z\right)\right]^n \\ \qquad\qquad -UA\left(T-T_e\right) \\ \dfrac{dz}{d\bar{t}} = k_0 e^{\left(-\frac{E}{RT}\right)} \left(C_0\right)^{n-1} \left(1-z\right)^n \end{cases} \tag{1}$$

with the initial conditions:

$$\begin{cases} T = T_0 \\ z = 0 \end{cases} \quad \text{at} \quad \bar{t} = 0 \tag{2}$$

The system above can be rewritten in a dimensionless form:

$$\begin{cases} \dfrac{d\theta}{d\tau} = \psi\left(1-z\right)^n \exp\left(\dfrac{\theta}{1+\varepsilon\theta}\right) - \theta = F_1\left(\theta, z\right) \\ \dfrac{dz}{d\tau} = \dfrac{\psi}{B}\left(1-z\right)^n \exp\left(\dfrac{\theta}{1+\varepsilon\theta}\right) = F_2\left(\theta, z\right) \end{cases} \tag{3}$$

with the initial conditions:

$$\begin{cases} \theta = \theta_0 \\ z = 0 \end{cases} \quad \text{at} \quad \tau = 0 \tag{4}$$

For the system under analysis the values of the parameters are given in Table 1.

The kinetic expression applied is the one by Duh et al. (1997):

$$-\frac{dC_{CHP}}{dt} = k_0 \exp\left(-\frac{E}{RT}\right)\sqrt{C_{CHP}} \tag{5}$$

Criteria for Runaway Detection and Sensitivity Analysis

Among the various methods developed to detect and prevent the phenomenon of thermal runaway the method suggested by Strozzi and Zaldivar (1994) is based on the divergence of system (3) which has to be negative to avoid hazardous conditions; in other words, if the divergence becomes positive on a segment of the reaction path, the system is sensitive.

Table 1. The reaction parameters

Items	Values
CHP wt%	80
ρ (kg/m^3)	1016.3
$\hat{C}_p$ (kJ/kg/K)	2.219
-$\Delta\hat{H}_R$ (kJ/kg)	1500.0
k_0 ((mol/m3)$^{0.5}$/s)	5.632e12
E (kJ/mol)	122.0
n	0.5

To perform a parametric sensitivity analysis for the batch reactor under study we can assign a set of similar (something like indistinguishable) initial states integrating the system (3) in general form for all of these. If the different trajectories diverge before reaching the final state, the system is called sensitive; if they collapse onto a unique trajectory the system is not sensitive and initial uncertainties do not influence the behavior of the system.

In order to quantify the divergence of initial nearby states, let's take a set of initial similar states lying in certain region of phase space and denote with V(0) the volume of this region. Now, let these initial conditions evolve under the action of the nonlinear system, describing a set of trajectories. It is possible to follow the evolution of the initial volume V(0); adopting a strong version of Liouville's theorem we find that:

$$\frac{dV(t)}{dt} = \int_0^t tr\left(\boldsymbol{J}\left(\theta, z\right)\right) d\theta dz \tag{6}$$

where the trace of the Jacobian of the system (3) is a scalar quantity defined at each time and called divergence:

$$tr\left(\boldsymbol{J}\left(\theta, z\right)\right) = \frac{\partial F_1}{\partial \theta} + \frac{\partial F_2}{\partial z} = div\left(\boldsymbol{F}\left(\theta, z\right)\right) \tag{7}$$

If the initial n-dimensional volume V(0) was small enough related to the n-dimensional space in which the system evolves, the divergence of the vector field can be considered constant over V(t) and after few steps it is possible observe that the initial volume V(0) can shrink or grow with time in R^n as:

$$V\left(t\right) = V\left(0\right) \exp\left[\int_0^t tr\left(\boldsymbol{J}\left(\theta, z\right)\right) d\tau\right] \tag{8}$$

So, if $tr\left(\boldsymbol{J}\left(\theta,z\right)\right)=div\left(\boldsymbol{F}\left(\theta,z\right)\right)>0$ for all θ, z on a segment of the reaction path, the flow of the trajectories in the phase space is volume expanding and near initial conditions tend to diverge and behave quite differently. In the opposite case the volume is contracting during the evolution of the system and near initial conditions tend to converge to a unique trajectory.

When dealing with batch systems, we are not interested in the final state for $\bar{t}\to\infty$ but we have to observe the dynamic of the orbital collapse, because, before reaching the final state, trajectories can diverge.

For a batch system the divergence is:

$$div\left(\theta,z\right)=\psi\left(1-z\right)^{n-1}\exp\left(\frac{\theta}{1+\varepsilon\theta}\right)\left[\frac{1-z}{\left(1+\varepsilon\theta\right)^{2}}-\frac{n}{B}\right] \tag{9}$$

and to prevent runaway the condition is:

$$div\left(\theta,z\right)<0 \tag{10}$$

The divergence method has been compared with Velo et al. (1996) method that is based on the locus of temperature maxima.

From the conservation equations (3) and kinetic expression (5) for the system it is possible to obtain the following expression:

$$\frac{d\theta}{dz}=B-\beta\theta\frac{\exp\left(-\dfrac{\theta}{1+\varepsilon\theta}\right)}{\sqrt{1-z}} \tag{11}$$

where *B* is the heat generation potential and *β* the cooling intensity.

On the basis of the analysis of the parameter values a safety criterion which requires the computation of the temperature maxima locus is developed setting $\frac{d\theta}{dz}=0$.

From the correlation:

$$z_{max}=1-\left(\frac{\beta}{B}\right)^{2}\theta_{max}^{2}\exp\left(-\frac{2\theta_{max}}{1+\varepsilon\theta_{max}}\right) \tag{12}$$

which only depends on Semenov Number $\psi=\frac{B}{\beta}$ and ε, it can be seen that for small values of ψ the locus of maxima intercepts the y-axis, i. e. $z_{max}=0$, in two points, θ_a and θ_b with $\theta_a<\theta_b$. In this case, if the batch reactor works with an initial dimensionless temperature θ_0 less than θ_b, the mass temperature can also reach a maximum but its value is bounded. Critical is the situation that occur when $\theta_0>\theta_b$ because the temperature rises continuously before crossing the locus of maxima. On the other hand for large values of ψ no point can be found for $z_{max}=0$ and therefore for every value of ψ there is a critical value of B above which the system temperature runs away.

Results and Conclusions

Fig. 1 reports the initial divergence value vs. the initial temperature T_0. It is evident how, for T_0 >82°C, divergence is positive and runaway occurs according to Strozzi and Zaldivar method. The external temperature T_e does not influence results for $\bar{t}=0$, which seems reasonable.

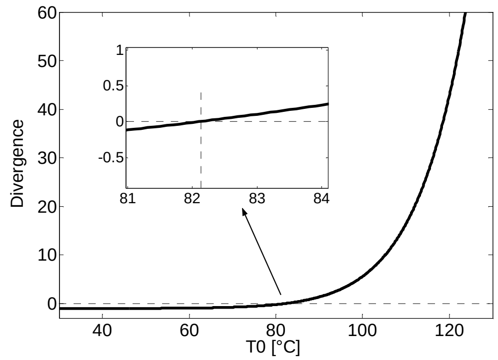

Figure 1. Initial divergence values vs. T_0 ($V = 200\ m^3$).

Below 82°C the divergence method can be applied studying the system evolution and computing the divergence at each integration step (equation (3) can be conveniently integrated by means of a 4th order Runge-Kutta method). For $T_0<82°C$ (see fig. 2) the critical external temperature (i.e. T_e above which divergence becomes positive during time evolution) does not sensibly vary with volume (about 10 °C for a volume change of about 1000 m^3) as well as with initial temperature (in fig. 2 two curves corresponding to $T_0=80°C$ and $T_0=10°C$ are reported).

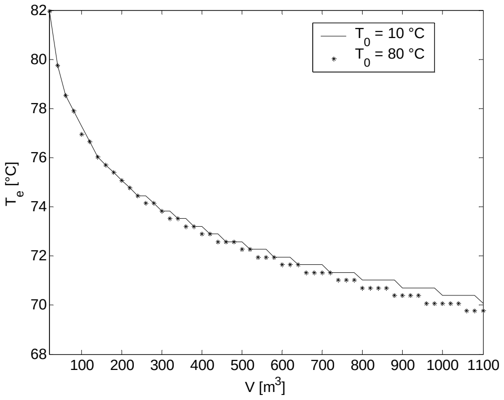

Figure 2. Critical T_e vs. V (divergence method).

The limit of about 82°C found applying the divergence method (that proves more conservative) is not respected by Velo et al. method, whose results are shown in the diagram of fig. 3 for V = 200 m^3.

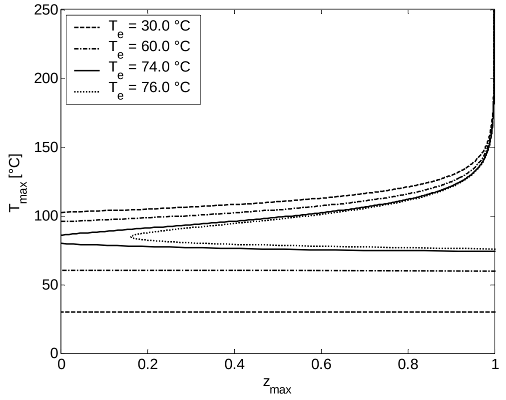

Figure 3. Loci of maxima for V = 200 m^3 (Velo et al. method).

For T_e lower than the critical one, that according to fig. 2 ranges from about 80°C to 70°C, it is possible to use a T_0 up to 100°C: for instance for $T_0 = 100°C$ and $T_e = 30°C$ the operation is still safe as confirmed by simulation results of fig. 4.

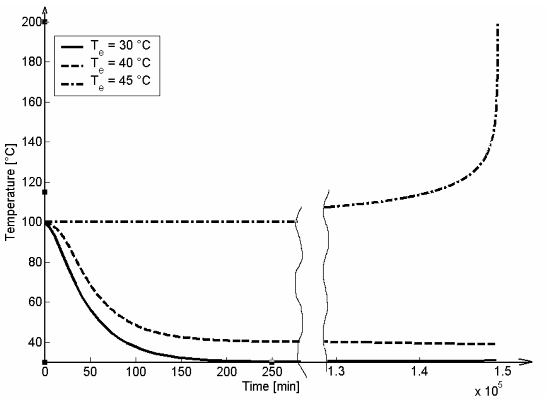

Figure 4. Simulation results for T_0 = 100°C and V = 200 m^3 (T_e = 30°C, 40°C, 45°C).

Nomenclature

A = heat transfer area, m^2
C = reactant concentration, mol/m^3
$\hat{C}_p$ = average heat capacity of reactant mixture, kJ/kg/K
$-\Delta H_R$ = heat of reaction, kJ/mol
$\Delta T_{ad} = \frac{(-\Delta H_R)C_0}{\rho \hat{C}_p}$ = adiabatic temperature rise, K
E = activation energy, kJ/mol
k_0 = pre-exponential factor of Arrhenius equation, (mol/m^3)$^{0.5}$/s
n = reaction order
R = universal gas constant, J/mol/K
$\bar{t}$ = time, s
T = mixture temperature, K
T_e = jacket temperature, K
U = overall heat transfer coefficient, W/m^2/K
V = reactor volume, m^3
ρ = density, kg/m^3

Dimensionless parameters

$B = \frac{\Delta T_{ad}}{T_e \varepsilon}$ = dimensionless adiabatic temperature rise
$\beta = \frac{UA}{V \rho \hat{C}_p k(T_e) C_0^{n-1}}$ = dimensionless heat transfer coefficient
$\varepsilon = \frac{RT_e}{E}$ = dimensionless jacket temperature parameter
$\theta = \left(\frac{T - T_e}{T_e}\right)\frac{E}{RT_e}$ = dimensionless temperature
$t = \bar{t}\psi$ = dimensionless time
$\tau = \bar{t}\,\frac{UA}{V \rho \hat{C}_p}$ = dimensionless time

$\psi = \frac{B}{\beta}$ = Semenov Number

$z = \frac{C_0 - C}{C_0}$ = reactant conversion

subscript

e = coolant or ambient
max = maximum
0 = initial condition

References

Bosch C. M., Velo E., Recasens F. (2001). Safe storage temperature of peroxide initiators: prediction of self-accelerated decompostion temperature based on a runaway heuristics. *Chem. Eng. Sci.*, **56**, 1451-1457.

Duh Y. S., C. S. Kao, H. H. Hwang and W. L. L. Lee (1997). Thermal decomposition kinetics of cumene hydroperoxide. *Trans I. Chem. E.*, **75B**, 73-78.

Pellegrini L., S. Bonomi and G. Biardi (2003). Dynamic simulation of the cleavage section in a phenol plant for safety analysis. *Proceedings of FOCAPO*, Coral Springs, Florida.

Pellegrini L., S. Bonomi and G. Biardi (2003). Identification of risk scenarios in the phenol-acetone process. Part I: The cumene oxidation unit. *Proceedings of AIChE 37th Annual Loss Prevention Symposium*, New Orleans, LA.

Strozzi F. and J. M. Zaldivar (1994). A general method for assessing the thermal stability of semibatch processes based on Lyapunov exponents. *Chem. Eng. Sci.*, 2681.

Velo E., Bosch C. M., Recasens F. (1996). Thermal safety of batch reactors and storage tanks. Development and validation of runaway boundaries. *Ind. Eng. Chem. Res.*, **35**, 1288-1299.