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Dynamic modeling and bifurcation analysis for the methyl isocyanate hydrolysis reaction

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ABSTRACT

The aim of this work was to characterize the methyl isocyanate hydrolysis reaction and to identify its operational criteria. The parametric sensitivity and dynamic stability methodologies were performed at the Bhopal disaster circumstances, over the relevant operating parameter space. Stable and unstable conditions, bifurcations points, turning points and oscillatory behavior were determined. The combined methodology give useful guidance on the operative conditions selection and the appropriate strategy to overcome hazardous situations. The obtained results demonstrated high sensitivity to small perturbations (thermal runaway) and prevalent oscillatory behavior. Moreover, the following critical parameters for the studied dynamic system were defined: the inverse residence time of 1.5700103 and the heat transfer coefficient of 752.394.

1. Introduction

Methyl isocyanate (MIC) is an intermediate product in carbaryl production, chiefly used as an insecticide. MIC is a highly toxic and irritating substance, it is extremely hazardous to human health. It was the principal chemical involved in the Bhopal disaster, the history's worst industrial accident (Mishra et al., 2009). The tragedy occurred in the Union Carbide pesticide plant in Bhopal, India. On December 2, 1984, water inadvertently entered to the storage tank containing more than 80,000 pounds of MIC. A subsequent runaway reaction overheated the tank and resulted in a massive toxic gas release. A dense, lethal cloud drifted over the city of Bhopal exposing hundreds of thousands of people to deadly MIC and other chemicals. Nearly 8000 people died initially and approximately 20,000–30,000 people in total (Eckerman, 2005; Varma and Varma, 2005; Kletz, 2009). Investigations found many deficiencies in the process safety management, among them: the absence of a process hazard analysis, poorly maintained equipment and safety systems, a lack of emergency response planning, inadequate training and fundamental faults within the educational preparation of operators handling the deadly MIC (Kletz, 2009; U.S. Chemical Safety and Hazard Investigation Board, 2015a).

The Bhopal incident and many other chemical accidents have resulted in a series of recommendations, on preventive procedures or continuously reducing process risks, for chemical engineering educators, industrial operators and organizations, labor groups, and regulatory agencies. They include enhancing safety regulations in the chemical industry (U.S. Chemical Safety and Hazard Investigation Board, 2015b CSB video), and adding reactive hazard awareness to baccalaureate chemical engineering curricula (Sache, 2015). In relation to these last aspects, much more needs to be done to assure that future tragedies will be avoided. Safety considerations must become essential components in the analysis, design, and operation of process equipment.

Dynamic modeling and simulation are important tools for hazard process assessment (Ball, 2013; Elnashaie and Uhlig, 2007). The parametric sensitivity analysis is frequently used to identify hot spots and runaway criteria (for preliminary screening purposes) (Luo et al., 2002; Maria and Stefan, 2010; Maria and Dan, 2012), while the stability analysis helps to track oscillatory behavior (how the reactive system responses to a small perturbation). They allow identifying operational limit conditions. The stability analysis, using the well-founded stability theory, is undoubtedly

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recommended for reactive system studies (Ball and Gray, 2013). In fact, any conclusion made only basing on parametric sensitivity analysis (classical ignition theory) is pointless. Recently, Ball (2011) has published a notable analysis on the oscillatory thermal instability of the hydrolysis of MIC, at Bhopal disaster conditions. She has concluded that the thermal runaway occurred due to oscillatory instability rather than a steady state turning point.

The objective of this research is to gain insight into the MIC reaction. Both parametric sensitivity and stability analysis are employed to characterize the reactive system and identify operational criteria, more precisely, mapping the operating environment. The reactive system is solved at conditions as these reported for Bhopal catastrophe. Subsequently, the geometry of temperature profiles are analyzed and critical conditions are defined. Finally, they are compared with the results obtained for the rigorous dynamic analysis (unstable conditions, bifurcations points, turning points and oscillatory behavior). This methodology provides useful guidance on different reactive problems that may appear in the industrial practice and the appropriate strategy to overcome them.

2. Reactive system

MIC (CH_3NCO) hydrolysis is a highly exothermic reaction (heat of reaction, $\Delta H_{rxn} = -80.4$ kJ/mol). It generates methylamine (CH_3NH_2) and carbon dioxide (CO_2) as products:

$$CH_3NCO_{(1)} + H_2O_{(1)} \xrightarrow{k_1 T} CH_3NH_{2(aq)} + CO_{2(aq)} \quad (1)$$

where $k_1(T) = Aexp(-E_a/(R.T))$, A is the frequency factor (4.13×10^8 s^{-1}), E_a is the activation energy (65.4 kJ/mol), R is the ideal gas constant (kJ/mol.K), and T is the temperature (K) (Ball, 2011). It has been also reported that MIC and methylamine can react to form dimethyl urea ($CH_3NHCONHCH_3$) (D'Silva et al., 1986), as follows:

$$CH_3NCO_{(1)} + CH_3NH_{2(aq)} \xrightarrow{k_2(T)} CH_3NHCONHCH_{3(aq)} \quad (2)$$

In this work, only thermal instability generated by Reaction (1) is considered due to the lack of experimental kinetic data related to the Reaction (2).

3. The dynamic model for thermal instability analysis of MIC hydrolysis

Ball (2011) modeled and simulated the MIC hydrolysis reaction in a large storage tank as a dynamic Continuous-Stirred Tank Reactor (CSTR). This mathematical model seems to be appropriate for the case of Bhopal incident since, in a time interval, the reactive volume can be assumed as constant and the concentration gradients negligible in comparison to the increase in the reaction rate (Ball, 2011). Thus, the following differential equations describing the change of mass and temperature with time are:

$$m\frac{dc}{dt} = -mAe^{-E_a/RT}c + F(c_0 - c) \quad (3)$$

$$mC_{P,0}\frac{dT}{dt} = (-\Delta H_{rxn})mAe^{-E_a/RT}c + F\left(C_{P,0}T_a - C_P T\right) - L(T - T_a) \quad (4)$$

where m is the MIC mass (kg), c is the MIC concentration (mol/kg), t is the time (s), F is the mass flow (kg/s), L is the heat transfer coefficient (W/K), and Cp is the mixture specific heat (J/(kg.K)) evaluated using the correlations from Yaws (2015). The subscripts 0 and a indicate feed and ambient conditions, respectively. The balances (3) and (4) present the following initial conditions:

$$t = 0, \quad c = c_0, \quad T = T_0 \quad (5)$$

For the numeric solution and stability analysis convenience, the following dimensionless variables and parameters are introduced:

$$u = \frac{c}{c_0} \quad \text{Dimensionless MIC concentration} \quad (6)$$

$$\theta = \frac{RT}{E_a} \quad \text{Dimensionless reactive temperature} \quad (7)$$

$$\tau = A't \quad \text{Dimensionless time} \quad (8)$$

$$f = \frac{F}{mA'} \quad \text{Dimensionless flow} \quad (9)$$

$$\theta_a = \frac{RT_a}{E_a} \quad \text{Dimensionless cooling temperature} \quad (10)$$

$$\ell = \frac{LE_a}{mA'c_0(-\Delta H_{rxn})R} \quad \text{Heat transfer term} \quad (11)$$

$$\varepsilon = \frac{C_P E_a}{c_0(-\Delta H_{rxn})R} \quad \text{Heat generated term} \quad (12)$$

$$\gamma = \frac{C_{P,0}}{C_P} \quad \text{Specific heat relation} \quad (13)$$

where A' corresponds to a modified frequency factor, defined as $A' = Ae^{-1/\theta_s}$, and θ_s is a dimensionless temperature scaling factor, defined as $\theta_s = RT_s/E_a$. The T_s has a constant value of 292 K. Thus, the dimensionless mass and temperature equations may be written as follows:

$$\frac{du}{d\tau} = -ue^{1/\theta_s - 1/\theta} + f(1 - u) \quad (14)$$

$$\varepsilon\frac{d\theta}{d\tau} = e^{1/\theta_s - 1/\theta}u + \varepsilon f(\gamma\theta_a - \theta) - \ell(\theta - \theta_a) \quad (15)$$

Whose initial conditions adopt the following form:

$$\tau = 0, \quad u = 1, \quad \theta = \theta_0 \quad (16)$$

Thus, the model to analyze the thermal stability of MIC hydrolysis reaction is represented by the set of two dimensionless differential Eqs. (14) and (15), and includes five dimensionless parameters (f,ε, γ, ℓ and θ_a). At the Bhopal incident conditions, they presented the following values: $f = 1.7$, $\gamma = 1$, $\varepsilon = 10$, $\theta_a = 0.0379$, and $\ell = 700$ (Ball, 2011). They will serve as reference for simulation analysis.

4. Numerical tools for dynamic analysis

The system steady states for a particular set of parameters were calculated using Matlab®. Its ordinary differential equation (ODE) solvers (built-in routines) are not efficient to find all the roots of the dynamic model. Thus, these steady states were used as the initial point for the numerical bifurcation analysis using Matcont (http://www.mathworks.com/matlabcentral/). For simulations, initially